

CHEMICAL ABSTRACTS

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I—APPARATUS

C. G. DERRICK

Improvements in the Soxhlet extraction apparatus. OSKAR HAGEN. Dresden. *Chem.-Ztg.* 45, 19(1921); 1 cut.—The siphon is eliminated, the solvent returning to the boiling flask through the main tube under the extraction chamber. This tube is bent in a vertical loop between the extraction chamber and the point where the vapor tube is attached, the loop forming a seal against the vapor. On the outer side of the loop a stopcock is inserted, the cock being so bored that in 1 position it allows the condensate to return to the flask, but when turned 180° a sample of the condensate may be withdrawn to find if the extn. is complete. A funnel may be placed under the cooler, if desired, to drop the condensate in the middle of the extn. thimble. J. H. MOORE

Distilling apparatus for small quantities. CARL WOYTACEK. Hamburg. *Chem.-Ztg.* 45, 82(1921); 1 cut.—A 100-cc. Erlenmeyer flask carries a vertical double-walled condenser, the vapor from the flask being delivered, through an internal pipe, at the top of the inner chamber and the condensate withdrawn through a tube at the bottom of this chamber. J. H. MOORE

Contrivance to prevent water sucking back from water vacuum pumps. HANS DORSCH. Chem. Inst. Würzburg. *Chem. Ztg.* 45, 32(1921); 2 cuts.—The grip of a stout Geissler stopcock is fastened in a cork with sealing wax and the cork held in a clamp so that the hole through the body of the cock is nearly horizontal, the small end of the body pointing slightly upward. The tube on 1 side of the cock is about 14 cm. long and is bent downward at about 45° near the end, the other arm being straight and about 9 cm. long. On the long end is a 2-hole stopper carrying a 250-300-cc. flask. Through the other hole a tube enters and bends downward to the lower side of the flask, the outer end being connected to the pump with a short piece of flexible vacuum hose. The short arm of the cock is connected to the desiccator by a flexible hose and carries a counter-wt. for the flask, which must be well adjusted, and the cock well greased. If the H₂O pressure drops, H₂O sucks back into the flask; this sinks and closes the cock. When the pressure rises again the H₂O is sucked out of the flask and the counter-wt. opens the cock. J. H. MOORE

W. Friedrichs' mercury-vapor pump. GREINER & FRIEDRICH. Stützerbach. *Z. angew. Chem.* 34, Aufsatzteil 46(1921); 1 cut.—Description of a small pump, operating with about 20 cc. Hg, which will produce in a 2-l. receptacle in 5 mins. a vacuum of 0.0001, and in 10 mins. a vacuum of 0.00001 mm. Hg, through a connection about 4 mm. long and 10 mm. diam. with cocks 4-5 mm. bore, when starting with a vacuum of 15-20 mm. Hg. J. H. MOORE

Schmidt's glass autoclave. ANON. *Chem.-Ztg.* 45, 131(1921); *Z. angew. Chem.* 34, Aufsatzteil, 37(1921); 1 cut.—A small vertical, cylindrical glass app. for carrying out reactions up to 60 lbs. pressure. It is held upright by a stand clamp, is heated in a paraffin-oil bath or by superheated steam, has 2 coolers on top and is connected with a pressure regulator. Made by L. Hormuth Co., Heidelberg. J. H. MOORE

A practical viscosity tester. HEINRICH MALLISON. Berlin. *Chem.-Ztg.* 45, 135(1921); 1 cut.—Designed for rapidly testing the viscosity of small amts. of oils with approx. accuracy, it consists of a broad base board set at a slight angle to the

horizontal, near the higher edge of which is hinged another board which may be clamped in a vertical position or folded back on the base board. On the front of the hinged board are 4 metal clamps for holding test-tubes. To operate, 1 of the tubes is filled with the oil to be tested to a mark about 2.5 cm. from the bottom, and another to the same height with an oil of known viscosity. The vertical board is then folded back on the base board and by comparing the rates of flow the viscosity of the sample is judged with reasonable accuracy.

J. H. MOORE

New attachments for the polarizing microscope. M. BEREK. *Wetzlar. Z. Kryst. Min.* 55, 615-26(1920).—Descriptions are given of convenient arrangements of Bertrand lenses and iris diaphragms for the study of interference figures, and of an improved Fedorov universal stage.

R. T. WHERRY

The refractometer in the factory laboratory. F. LÖWY. *Chem.-Ztg.* 45, 25-7, 52-5(1921).—A description of the various Abbé refractometers and their use in the fat and oil, sugar, and other industries. Largely a review of previous work with numerous references.

H. S. BAILEY

Indicators for carbon dioxide and oxygen in air and flue gas. L. H. MILLIGAN, D. O. CRITES AND W. S. WILSON. *Bur. of Mines, Tech. Paper* 238, 23 pp.(1920).—Construction and operation are described of portable instruments designed in the research lab. of the Pittsburgh expt. station. CO_2 is absorbed by NaOH ; O is absorbed by alk. pyrogallate. For details see the original.

JEROME ALEXANDER

An electric furnace for the separation of arsenic in Lockemann's method for determining arsenic. L. BIRCKENBACH. *Chem.-Ztg.* 45, 61-2(1921); 3 cuts.—L.'s method (*Z. angew. Chem.* 1905, 416) is improved by substituting an elec. furnace for Bunsen burners for heating the tube in which the mirror is deposited, by using a calibrated capillary tube, and by using a Zn-Cu alloy for evolving the H. The furnace (made by Desaga Co., Heidelberg) is made of diatomaceous earth and consists of an upper and lower half with a hole running lengthwise and lined with asbestos paper. The heating spiral of Cr-Ni steel of 1 mm. diam. lies in this channel, and the decomposition tube is pushed through the spiral when in use. A vertical hole near 1 end of the furnace allows a wool string to pass from a dish of H_2O above the furnace down around the capillary tube to a beaker below, to cool a section of the tube. The current must be such as to give a temp. of about 700° , 105 v. and 4 amps. being sufficient with the above spiral. The decomposition tube, of very high-fusing glass, consists of a section about 300 mm. long and 6 mm. inside diam., walls 1 mm. thick, ending in a capillary tube 160 mm. long, 1 mm. inside diam., walls 1 mm. thick. The alloy is made by fusing in a porcelain crucible 500 g. of purest As-free Zn and 0.625 g. purest Cu and granulating in H_2O . To operate, put 8-10 g. of the alloy in a 150-cc. flask with 25 cc. purest dil. H_2SO_4 (1:7) and let stand 25-30 mins., then push the tube through the spiral, adjust the wool string, turn on the current, thoroughly dry the projecting ends of the tube with an alc. lamp and ignite the escaping H. The H_2SO_4 soln. of the substance to be tested, which must be free from org. substances, sulfides, chlorides, nitrates, Se and oxidizing substances, is now added to the flask and the funnel washed down twice with about 30-cc. of the dil. H_2SO_4 . After 1 hr. the test is ended and the mirror is cooled in a current of H and compared with standards made under the same conditions with known amts. of As.

J. H. MOORE

Estimation of toxic water-soluble dust with the Palmer apparatus. MIRIAM STEWART ISZARO. *Univ. Penna. J. Ind. Hygiene* 2, 344-7(1921).—The Palmer dust-collecting app. may be used for the detn. of the presence of aniline attached to dust particles in the air by using a medium in which aniline is sol., e. g., 10% HCl soln. This app. may be used for the detn. of the count in air of dust particles which are sol. in distd. water by substituting a medium in which they are not sol., e. g., paraffin oil. The

app. may be used for the detn. of *total solids* in the air, by passing a known vol. of air through the medium, evapn. to dryness in a tared vessel, drying to constant wt., and thereby obtaining the wt. of solids. In the quant. detn. of *aniline* in air using this app., the longer the app. is run, the more accurate the results; sufficient aniline should be collected to permit at least duplicate titrations on each sample with NaNO_2 .

JOSEPH S. HEPBURN

Some thermal characteristics of electric ovens and hot plates. II. C. E. ALLSOP, *et al. Electrician* 86, 301-2(1921). C. G. F.

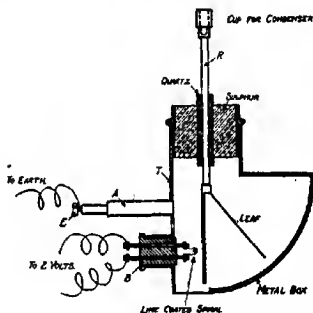
Air-oven thermo regulator. H. M. ATKINSON. *J. Soc. Chem. Ind.* 39, 298T (1920).—A loaded glass cylinder carrying at its upper end a capillary tube, floats in a U tube of Hg one arm of which is connected with the oven, the other arm having a side inlet for the gas. As the air in the tube inside the oven expands it raises the float, whose upper end enters a ground joint, thus cutting down the size of the exit for the gas from that arm of the U tube.

JEROME ALEXANDER

Shadow electroscope. R. WHIDDINGTON. St. John's College. *Proc. Camb. Phil. Soc.* 20, I, 109-15(1920).—In order

to eliminate optical systems from an electro-static voltmeter for lab. and instructional work, the shadow of the leaf was cast on a semi-transparent scale by the filament of a small 2-volt lamp. The tube T carries a S plug fitted centrally with a quartz tube down, which passes the rod R; this carries the leaf at its lower end and a small cup at the top. The metal arm A is for clamping and tilting purposes and carries an earthing terminal E. Below A a short side-tube carries an ebonite block B in which a small lime-coated spiral is fitted; the object of the latter is to provide a source of ions for expts. on ionization when heated by a 2-volt cell. The range of the app. is from 100 to 500 volts, with an accuracy of about 1 volt. The scale is calibrated by comparison with a standard voltmeter. Four lab. expts. on the measurement of capacity are described.

W. B. V.



Cement for mirror scales. FREDRICH POLLAK. Vienna. *Chem.-Ztg.* 45, 146 (1921).—P. mends a clean break in a glass scale as follows: The pieces are placed together scale side down on a smooth surface. The line of the break is covered with a layer 1 mm. thick of pieces of flower wire 1.5-2 cm. long. Marine glue is melted and poured over the layer of flower wires while the pieces of glass are gently pressed together. When the glue is nearly set, the scale may be taken up and any unevenness corrected. Marine glue alone is too brittle and sealing wax hardens too quickly for this purpose. Any glue on the front of the scale is removed by gentle rubbing with alcohol.

J. J. MORGAN

Standardizing of air drying chambers. H. GERBER. *Z. angew. Chem.* 34, Aufsatzteil, 7(1921); 2 cuts.—C. recommends 2 types of lab. air chambers. The 1st is a sheet-steel, double-walled dryer in which the hot air and gases from the burner pass through

small holes in the outer wall of the bottom and up between the walls to a number of exit holes on top. Instead of 2 tubes on top 3 are recommended. The chamber is suspended by means of 2 books, is covered with graphite instead of lacquer, and an easily replaceable Cu sheet is attached to the bottom where the flame strikes. The temp. in top and bottom should not be more than 3-4° apart. 3 sizes, of 28, 45 and 40 cm. height, 18, 28 and 50 cm. width, and 22, 28 and 35 cm. depth, respectively, are recommended. The 2nd type is a 3-walled sheet-steel chamber covered with asbestos, the gas jets being between the outer walls and the gases escaping through a central tube on top. Air circulates downward to the bottom then up between the inner walls, so that the upper shelf is the hottest. Galvanized wire gauze is recommended for shelves, and 2 tubes through the top. 3 sizes, of 30, 45 and 45 cm. height, 25, 28 and 60 cm. width, and 20, 28 and 30 cm. depth, respectively, are recommended.

J. H. MOORE

Ruggles-Coles dryer. H. JORDAN. *Feuerungstechnik* 9, 31-3(1920).—The construction and operation of various forms of Ruggles-Cole driers are discussed with photographs and drawings of the various classes. Also in *Chem. App.* 8, 32-4 (1921).

H. C. PARRISH

Efficient capacity of centrifugal pumps. H. A. WHITE. *J. Chem. Met. Soc. S. Africa* 21, 113(1920).—A table is given showing the number of cu. ft./min., gals./min., fluid in tons/hr., tons solid/hr. for pumps of varying delivery bore. The figures represent average practice but are sometimes exceeded by increasing speed of revolution and enlarging suction and delivery piping.

E. H. DARBY

The driving of centrifugals (BROADBENT) 13. Plastometer (GREEN) 26. Apparatus for the determination of hydrogen-ion concentration (VAN ALSTINA) 7.

Drying apparatus. K. BAN. Japan 36,196, April 15, 1920. The app. is composed of a long revolving tube.

Drying apparatus. T. IZUMI and Y. IZUMI. Japan 36,198, April 15, 1920 (Addition to 32,526). Drying is performed by circulating hot air.

Drying apparatus. T. IZUMI and Y. IZUMI. Japan 36,199, April 15, 1920. Hot air is circulated downwards and a beater is placed in the middle part.

Powder-drying apparatus. S. MATSUSHITA. Japan 36,089, April 6, 1920. Pasty finely divided material is painted on an endless band of wire gauze and dried by revolution.

Continuous constant-temperature distilling apparatus. J. SAKASHIMA. Japan 36,082, April 6, 1920. Fractional distn. is conducted by one operation.

Apparatus for separating air into its components. K. SOGA. Japan 36,065, April 5, 1920. Liquid air is sepd. into O₂, N₂, Ar and Ne by evapn.

2—GENERAL AND PHYSICAL CHEMISTRY

W. E. HENDERSON

Recent advances in science—physical chemistry. W. E. GARNER. Univ. London. *Sci. Progress* 15, 373-7(1921).—Review of recent work on: (a) the third law of thermodynamics and the entropy of solns. and liquids, (b) lubrication and chem. constitution, and (c) colloidal electrolytes. Cf. C. A. 15, 194.

JOSEPH S. HEPBURN

Investigations of the chemical literature. FRANK E. BARROWS. *Chem. Met. Eng.* 24, 423-8, 477-9, 517-21(1921).—A valuable general survey of methods and facilities. Library facilities, general reference books, the periodical literature, indexes, patents, etc., are discussed. The importance of proper training and guidance in making investigations of the chemical literature is emphasized.

E. J. C.

Chemical retrospect and prospect. H. GOLDSCHMIDT. *Pharm. Monatshefte* 1, 160-1(1920).—An address. W. O. E.

Universality of any given state as consequence of the fundamental law of energetics. P. P. VON VEDMARN. *Ann. école mines Oural Institute* 1, Part 2, 1-3(1919).—Accepting Ostwald's view that matter is merely a spatial aggregation of different varieties of energy, and in view of the fundamental law that these varieties are mutually convertible, W. comes to the conclusion that it ought to be possible to convert the chem. elements into each other, the problem reducing itself to finding the conditions for realization of any given state. Thus, under the Na state all elements should change to Na; under the Au state they should change to Au, etc. H. M. GORDIN

The state of aggregation of the elements and the atomic model. F. A. HENGLER. Danzig. *Z. Elektrochem.* 27, 28-30(1921).—The state of aggregation of the elements has been represented with the aid of Stark's theory of inter-mol. and intra-mol. unions and Kossel's at. model. It is shown that the electrostatic attractive forces between the positive nucleus of an atom and its own valence electrons increase in the horizontal rows and decrease in the vertical columns of the periodic system as the at. number increases. The attractive forces between atoms behave in a similar manner. In the 1st 4 vertical columns of the periodic system the forces effect only inter-mol. unions, as evidenced by the monat. character of these elements; while in columns 5-7 of the periodic table the forces bring about the formation of elementary mols., there remaining over, however, sufficient forces for inter-mol. unions. In the case of the inert gases the forces acting between the positive nucleus and the valence electrons bring about a new configuration by drawing these electrons into the inner electron system. Since only weak mol. forces are present, these elements remain gaseous even at low temps.

H. JERMAIN CREIGHTON

An outline of the application of the theory of space groups to the study of the structure of crystals. RALPH W. G. WYCKOFF. *Geophys. Lah. Am. J. Sci.* [5] 1, 127-37(1921).—This is an attempt to give those details of the theory of space groups (and no more) that seem necessary in order that the results of this theory may be used in studying the structures of crystals. The general nature of the modifications of these results that are required in order that they may serve as the basis for a more general method of studying crystal structures are also outlined. R. W. G. W.

Determination of the structure of crystals. RALPH W. G. WYCKOFF. *Geophysical Lab. J. Franklin Inst.* 191, 199-230(1921).—This paper "aims to give a brief survey of the field of the detn. of the structures of crystals as it exists at the present time. The most essential events in the development of this work are mentioned, the existing means of experimentation are outlined, and some of its present limitations are discussed together with some of the kinds of problems to which a knowledge of the arrangement of the atoms in crystals has contributed and may be expected to contribute."

JOSEPH S. HEBURN

Recent advances in science—physics. F. T. PIERCE. *Sci. Progress* 15, 367-72 (1921).—Review of recent work on X-ray reflection from crystal powders, and on the magnetic properties of crystals.

JOSEPH S. HEBURN

A new crystalline form of potassium chlorate. E. R. WOLCOTT. *J. Ind. Eng. Chem.* 13, 215-6(1921).—Crystals of KClO_3 , having a fibrous silky appearance and apparently of prismatic habit (as distinguished from the more common tabular habit) can be grown from a soln. containing sol. hydrocarbons such as are obtained from crude petroleum.

RALPH W. G. WYCKOFF

The crystal structure of magnesium oxide. RALPH W. G. WYCKOFF. *Geophys. Lah. Am. J. Sci.* [5] 1, 138-52(1921); cf. Davey and Hoffmann, *Phys. Rev.* 15, 333 (1920).—An attempt is made to get a unique soln. for the structure of MgO as an ex-

ample of the application of the more general method of studying the structures of crystals which arises from the use of the theory of space groups. With the aid of X-ray spectrum measurements and Laue photographs it is shown that the "sodium chloride" arrangement is the only simple one that is possible, though there are more complicated groupings that agree equally well with the existing data. R. W. G. W.

Surface tension and heat of vaporization. W. HERZ. Univ. Breslau. *Z. Elektrochem.* 27, 25(1921); cf. *C. A.* 14, 672.—From Trouton's rule and Eötvös' equation the following relation between the surface tension (γ) and the heat of vaporization (L) of non-associated liquids at the b. p. has been derived: $L = 20\gamma/s^{2/3}M^{1/3}$. Values calcd. for a number of organic liquids by means of this equation agree fairly well with those obtained by expt. The equation can also be employed to calc. the mol. diameter ($\rho = 2\gamma\sigma/L$) and the internal pressure ($B = [10\gamma/(Mv)^{2/3}] \times 42700/1033$ atm.). The internal pressure equation gives for C_6H_6 , $CH_3CO_2C_2H_5$ and $C_4H_9NH_2$ the values 1830, 1425 and 2120 atms., resp. H. JERMAIN CREIGHTON

Heat of vaporization and critical data. W. HERZ. Univ. Breslau. *Z. Elektrochem.* 27, 26(1921); cf. preceding abstract.—The following formula has been derived, by means of which the heat of vaporization (L) of non-associated liquids at the b. p. can be calcd. from the crit. pressure (p_k), the crit. d. (d_k), the crit. temp. (T_k) and the b. p. (T): $L = p_k T / T_k d_k = 0.00093 T / d_k v_k$, where v_k is the crit. vol. Results obtained

Some notes on calcium. P. H. BRACE. *J. Inst. Metals* 1921, adv. copy No. 2, 16 pp.—A historical review divides the priority for the isolation of Ca among Davy, Berzelius and Pontin. After reviewing literature dealing with uses of Ca (alloys, etc.) a detailed description is given of some successful methods for prepg. Ca, including the submerged-cathode app. of Borchers and Stockem and the "contact cathode" of Rathenau with the authors modification for controlling the anode area. The prepn. of electrolytes is described. Also in *Engineering* 111, 308-10(1921). JEROME ALEXANDER

Helium: its history, properties, and commercial development. RICHARD B. MOORE. U. S. Bur. Mines. *J. Franklin Inst.* 191, 145-97(1921).—An account is given of the history and properties of He, and of the process used for its recovery from natural gas on a com. scale. Sections are devoted to the detn. of the He content of natural gas, the origin of He in natural gas, the com. storage of He, and the cryogenic lab. JOSEPH S. HEPBURN

Decomposition pressure of the saturated aqueous solution of ammonium bicarbonate. KYOSUKE NISHIZAWA. *J. Chem. Ind. (Japan)* 23, 830-45(1920).—In connection with the study of equil. in the NH_3 -soda process, N. measured the decompn. pressure of NH_4HCO_3 . The total pressure of the gas phase coexisting with satd. aq. soln. of NH_4HCO_3 is measured, having gas phase so small at the beginning that it is negligible in comparison with the vol. of the soln. taken. The results are: at 5° , 675; 10° , 948; 15° , 1397; 25° , 2665; 30° , 3620; 35° , 4924; 40° , 6923. The pressure is expressed in mm. of Hg. The relation between temp. and decompn. pressure is formulated as $\log P = 2.55169 + 0.0499125t - 0.0008515t^2 + 0.0000102266t^3$. S. T.

The compressibility of diamond. L. H. ADAMS. Washington, D. C. *J. Wash. Acad. Sci.* 11, 45-50(1921).—The diminution in vol. of clear colorless diamond chips when subjected to high hydrostatic pressures (10,000 megabars) was measured by the method already described (cf. *C. A.* 13, 391) and found to be 0.16 part per million per megabar. Diamond thus has the lowest compressibility of any known substance. Tungsten, the next in order of compressibility, is nearly twice as compressible as diamond. From a consideration of certain formulas connecting the physical properties of solids, it is shown that the low compressibility of diamond is in harmony with its high melting point, its low expansion coefficient, and its high atomic frequency. L. H. A.

An approximate calculation of the heat of fusion of the inert gases. J. HARBUTT. *Physik. Z.* 22, 52-3(1921).—For elements of the same group in the periodic table, the heat of fusion divided by the abs. m. p. is approx. a const. From the exptly. detd. values for A found by Eucken, the heats of fusion in Cal. per g. atom are calcd. to be for He < 0.004; Ne, 0.08; Ar, 0.268; Kr, 0.33; Xe, 0.43; Rn, 0.65. The value for He is lower than for any other known substance. E. N. BUNTING

The antagonistic action between ions of the same charge. S. M. NEUSCHLOSS. Budapest. *Kolloid-Z.* 27, 292-306(1920).—With increasing concn. of the chlorides of the alkalis, alk. earths and Al the surface tension of lecithin solns. passes through a max. then slowly decreases. The same salts exert a retarding effect on the inversion of cane sugar by invertase, which effect increases with the concn. of the salt and with the valence of the cation. The influence of the salt on the fermentation is parallel with its effect on the dispersity of the ferment soln.; therefore, the retardation of fermentation is due to the reduction of the active ferment surface in the microheterogeneous system. Mixtures of these salts show an antagonistic effect both on the surface tension of lecithin and on the fermentation and the surface tension of a ferment soln. This effect is dependent on the relative concn. of the cations and not on their absolute concn. and is probably a result of the tendency of one ion to drive the other ion from its adsorption compn. on the surface of the colloid particle, without itself replacing it. The relative concns. in which the salts are most antagonistic depend on the valence of the cation; for

univalent ions it is 1:1, for univalent to bivalent it is 20:1, for univalent to tervalent it is 100:1. One exception to this rule is in mixtures of Na and K, when maximum antagonism occurs with Na:K = 20:1 or 1:20.

H. I. MATTIL.

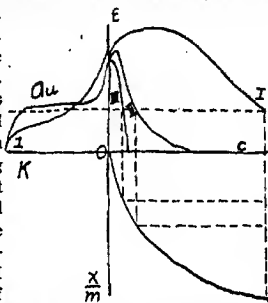
The irregular series of flocculation. H. R. KRUYT AND MADAME H. G. VAN ARKEL-ADRIANI. van't Hoff Lab., Utrecht. *Rec. trav. chim.* 39, 600-14(1920).—The purpose of these expts. was to det. which of the 2 theories concerning the irregular series is correct. The one puts the phenomenon in relation with reciprocal flocculation of colloids, the other is connected with the special behavior of the potential curve of the surface limit concn. of the electrolyte. The old expts. of Biltz (*Ber.* 37, 1115(1904)) support the former theory, but K. and v. d. Spek (*C. A.* 14, 1472) have found two cases of irregular series in which the older theory failed. In this paper systems in which a hydrolytic sepn. of a colloid of the opposite charge may play a role were investigated. For this purpose a Au sol. and $\text{Th}(\text{NO}_3)_3$ were selected. 90 cc. distd. H_2O + 10 cc. 3% H_2O_2 (dil. "perhydrol" accurately neutralized with NaOH) and 0.8 cc. of 0.66% HAuCl_4 were mixed and enough NaOH was added to neutralize the HCl formed (Groll, *C. A.* 10, 2322). Finally 1.4 cc. HAuCl_4 soln. was added. A double portion was mixed and divided into 2 parts. To one portion 1 cc. 0.08 N NaOH was added and examd. as the alk. sol (A); the other was the neutral sol (B). 5-cc. portions of these were treated with the $\text{Th}(\text{NO}_3)_3$ soln. Complete flocculation has occurred when the soln. becomes blue (Galecki, *C. A.* 6, 1411). These 2 Au sols were mixed with $\text{Th}(\text{NO}_3)_3$ at various concns. The primary limit value for flocculation of B was 0.00090 millimols. $\text{Th}(\text{NO}_3)_3$ per l. This flocculation ceased as the concn. was increased when a concn. of 0.0030 millimols. was reached. The blue color again appeared when 20 millimols. $\text{Th}(\text{NO}_3)_3$ per l. were present. With (A) these 3 values were 0.03, 0.10 and 5 millimols., resp. These results are remarkable in that (A) has limiting values about 33 times higher than (B). This suggests that the flocculating agent is not the same in the 2 cases, which is supported by the fact that with (A) the 1st zone of flocculation was indicated by red flakes instead of the characteristic blue color. ThO_2 was prepd. (Müller, *Koll. Z.* 2, 1 Suppl. VI (1907)) and when added to A gave red flakes at concns. of 0.25-0.50 millimols. per l. and red sols at lower and higher concns. It is concluded that the expts. with $\text{Th}(\text{NO}_3)_3$ on A and B each correspond to one of the above theories: for A it is a reciprocal pptn., for the 1st zone; with B the 1st zone of flocculation is explained by the neutralizing action of an oppositely charged ion. The general conclusion of the study is that in general the irregular series are produced by a strong electrocapillary action of the ions which are discharged. The reciprocal flocculation is observed only when a hydroxide is formed by making the soln. alk. Preliminary expts. with AlCl_3 give the same results. Other results were obtained with As_2S_3 sol (5 g. As_2S_3 per l.) and are briefly described.

E. J. WITZEMANN

The relation between the limit value and the concentration of gold sols. H. R. KRUYT AND A. E. VAN ARKEL. *Rec. trav. chim.* 39, 615-7(1920).—On the basis of researches on As_2S_3 sol., K. and v. d. Spek (*C. A.* 14, 1472) built a theory concerning the relation between the limit value and the concn. of sols of suspensoids. If the critical potential is independent of the concn. of the sol the equil. concn. of the electrolyte after adsorption ought to be const. for all dilns. of a colloidal system. As the amt. adsorbed decreases as the diln. of the sol is increased the less concd. sols should require less electrolyte to attain the desired potential. But as the diln. increases the chance for collisions in the sol is less and a lowering of the potential of contact necessary to produce a flocculating action of a given intensity occurs. For this reason dil. sols will require a higher concn. of electrolytes in the dispersive medium than in undil. sols. These 2 tendencies will vary in activity according to the nature of the flocculating ion. Thus with As_2S_3 with the K^+ ion the limiting value increases with diln., with Ba^{++} it rises

somewhat and with Al^{+++} it falls considerably. The limit value of nearly neutral Au sol (cf. preceding abstracts) as detd. by the appearance of the blue color with the undil. sol and 1:2 and 1:4 dilns. with H_2O . The results with KCl , $BaCl_2$, $AlK(SO_4)_3$ and $Th(NO_3)_4$ are given in tables. The results conform with those obtained with As_2O_3 . Higher concns. with diln. were required for the 1st 3 salts but the concn. of $Th(NO_3)_4$ required diminished with diln. of the Au sol. The irregular series was not obtained with $AlK(SO_4)_3$ nor with $AlCl_3$ but appeared at all 3 dilns. with $Tb(NO_3)_4$. E. J. W.

The critical potential. H. R. Kruv. *Rec. trav. chim.* 39, 618-22(1920).—Hardy's discovery that the flocculation of a colloidal sol occurs exactly at the concn. of the electrolyte that can stop the elec. cataphoresis led to the law concerning flocculation at the isoelec. point. Burton's expts. (*Phil. Mag.* [6] 17, 563(1909)) confirm H.'s results. Later K. (*C. A.* 9, 543) showed that complete discharge is not necessary for flocculation. Powis (*C. A.* 9, 737) found that the charge is diminished to a certain critical value. It should be possible to define this critical value at which flocculation is rapid and complete by describing the conditions at least. This involves the limit value, the contact potential, the critical potential and the probability of adhesion, which may be discussed graphically from the figure of Freundlich (*C. A.* 4, 2764). In this fig. I, II and III give the limit values of the flocculating ions of different valences represented on the axes ϵ and c . The curve on the axes ϵ and c gives the relation between the probability of adhesion and the charge at the limit surface. The probability of adhesion is the ratio of the no. of impacts that lead to a reunion to the total no. of impacts and varies from 0 to 1. It approaches 0 as the values for ϵ increase. At the iso-electric point it is no doubt 1. In the values between $\epsilon = 0$ and $\epsilon = \epsilon_{eq}$ there is little difference in the velocity of flocculation and this is shown by the convex curve $K - \epsilon$. But for Au sol (cf. preceding abstract) the curve will be more as indicated by the curve marked Au. The differences in these 2 curves represent the facts developed in the preceding abstracts. It is also shown how on the basis of the form of these 2 $K - \epsilon$ curves the results given for Au sol as well as those on As_2O_3 sol. referred to (preceding abstract) in the previous paper are to be expected. E. J. WITZEMANN



Coagulation of dispersoid solutions at the interfaces of phases. (Method of separation into layers and method of shaking.) A. YANEK. *Ann. école mines Oural* 1, 45-58(1919).—Two methods were used for coagulating dispersoid solns. at the interfaces of two liquid phases: (1) by shaking them with immiscible organic solvents (C_6H_6 , $CHCl_3$, Et_2O and CS_2) in sealed test-tubes, and (2) by pouring them into a homogeneous transparent mixt. of 1 vol. $CHCl_3$, 3 vols. H_2O and 4 vols. alc., or 3 vols. C_6H_6 , 1 vol. H_2O and 6 vols. alc. In (2) the addition of certain dispersoid solns. at once causes the transparent mixt. to become turbid like an emulsion. The degree of dispersion of the latter then gradually diminishes until finally the homogeneous mixt. seps. into 2 layers, at the interface of which the dispersoid phase is deposited as a thin film or in form of fine flakes. The results may be summarized as follows: The negative dispersoid solns. of As_2S_3 (obtained by passing H_2S into a soln. of $AuCl_3$), ZnS (obtained by passing H_2S into a suspension of $Zn(OH)_2$) and CuS (similarly obtained from a suspension of the ppt. produced by NH_3 in a soln. of $CuSO_4$) quickly and completely coagulate both by (1) and (2). The negative dispersoid soln. of Au (obtained by reducing $AuCl_3$ with $PhNHNH_2$) coagulates but slowly when shaken with C_6H_6 , and still more slowly when shaken with Et_2O ; but quickly and completely when shaken with CS_2 or $CHCl_3$, and by

(2). The positive dispersoid solns. of $\text{Fe}(\text{OH})_3$ (obtained by slowly heating a soln. of $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ to 80°) and $\text{Al}(\text{OH})_3$ do not coagulate either by (1) or (2). Method (2) was also applied to mixts. of mutually pptg. dispersoid solns. of Au (obtained by reducing AuCl_3 with tannin) and $\text{Fe}(\text{OH})_3$. It was found that there is an inverse ratio between the length of time these mixts. are capable of existing and the degree of completeness of coagulation (this degree being measured by the ratio of the amt. of coagulum to the total amt. of the dispersoid phase) and also an inverse ratio between the completeness of coagulation and the length of time required to complete the process. Hence there is a direct ratio between the "life" of these mixts. and the duration of the coagulation process. The "longevities" of these mixts. and the velocities of coagulation are given in tables. The coagulation by (2), and probably also by (1), is fractional. On this point expts. are in progress. When a washed finger is immersed in the dispersoid soln. of $\text{Fe}(\text{OH})_3$ the latter behaves like a negative dispersoid soln. both in (1) (shaken with CHCl_3) and (2). The same takes place when (1) is carried out not in sealed tubes, but in tubes closed with a washed finger.

H. M. GORDIN

The zone of maximum colloidal stability. Its relation to viscosity in hydrophilic colloids, especially Karaya gum and gelatin. JEROME ALEXANDER. *J. Am. Chem. Soc.* 43, 434-40 (1921).—Colloidal properties (e. g., viscosity) become more marked as the size of the dispersed particles increases from molecular subdivision (e. g., with soaps, nigh blue, butyric acid), and also as their size decreases from relatively coarse subdivision (e. g., in emulsions, homogenized milk). Expts. with Karaya gum show that fine grinding increases water-holding capacity and viscosity; on the other hand with soaps decrease in these factors is seen as the size of the fatty acid mols. decreases. Obviously there is a zone where they exhibit a max. As the dispersed phase becomes less viscous by swelling, the colloid as a whole becomes more viscous. With closely packed spheres the total adsorption space is const. but with large spheres there are relatively few large spaces, whereas with small spheres there are many small spaces, which means a big increase in surface forces.

JEROME ALEXANDER

Colloid chemistry and its general and industrial applications. F. G. DONNAN AND COMMITTEE. *Rept. Brit. Assoc. Advancement of Science* 1920, 1-154A; cf. *C. A.* 13, 1784.—The third of this series of excellent reports, including the following subjects: Soap, ultramicroscopy, soly. of gases in colloidal solns., elec. charge on colloids, imbibition of gels (tanning), bread making, photography (including collodion), cellulose esters, petroleum, asphalt, varnishes, paints and pigments, clays and clay products.

JEROME ALEXANDER

Ultramicroscopy: Degree of dispersion—measurement with the ultramicroscope. GEORGE KING. *Third Rept. on Colloid Chemistry, British Assoc.* 1920.—Discusses concn., size, shape, and internal structure of the dispersed phase, also a solid, liquid and gaseous continuous phase.

JEROME ALEXANDER

The solubility, rate of absorption and of evolution of gases, as influenced by colloids, with special reference to physiology and brewing. GEORGE KING. *Third Rept. on Colloid Chemistry, British Assoc.* 1920.—A suggestive review.

J. A.

The electrical charge on colloids. J. A. WILSON. *Third Rept. on Colloid Chemistry, Brit. Assoc.* 1920.—A brief discussion.

JEROME ALEXANDER

Imbibition of gels. J. A. WILSON. *Third Rept. on Colloid Chemistry, Brit. Assoc.* 1920.—A review including technical applications.

JEROME ALEXANDER

The measurement of the Brownian movement for a single particle. III. REINHOLD FÜRTH. Prague. *Ann. Physik* 63, 521-36 (1920); cf. *C. A.* 14, 486, 674, 3555.—Using the method of Ehrenhaft, F. investigates the motion of a charged Ag particle suspended in air under various exptl. conditions. In the case of a steady field, eB (the mean sum of the rate of fall and rate of rise divided by field strength when the field is

made of one sign and then of the other) is const.; for rapidly alternating fields eB , calcd. from the amplitude of the vibration, is const. and of the same order of magnitude. The accepted laws of the Brownian movement were verified. If, however, the charge on the particle is calcd. from the law of fall of Stokes or Cunningham, or from the law of the Brownian movement, the results for the Brownian and Stokes calcs. agree, while those for the Cunningham formula are much less. The lowest value of e is in the order of magnitude of the accepted value. Higher values, however, are not multiples of simple integers.

F. R. BRICHOWSKY

Studies in emulsions. II. Reversal of phases by electrolytes, and the effects of free fatty acids and alkalies on emulsion equilibrium. SHANTI S. BHATNAGAR. Univ. Coll., London. *J. Chem. Soc.* 119, 61-8(1921); cf. *C. A.* 14, 3555.—The effects of electrolytes on emulsion equil. in neutral oil and soap sols. have been studied with the view of elucidating the mechanism of emulsification. It has been shown that the reversal of phases is brought about more effectively by trivalent than by bivalent ions. The effect of diln. and of increasing the distance between the oil particles is essentially similar in nature to the effect of diln. on colloidal sols. The difference in the amount of electrolytes required to effect the reversal of phases with different soaps points to a difference in their protective actions. The results obtained indicate that for B. P. paraffin oil the soaps can be arranged in the order of their protective action as follows: $C_{18}H_{34}O_2K > C_{18}H_{34}O_2Na > C_{18}H_{34}O_2K$ and $C_{18}H_{34}O_2Na > C_{18}H_{34}O_2K > C_{18}H_{34}O_2Na$. The bearing of these results on the chem. interpretation of the *washing power of soaps* is considered briefly, and it is pointed out that their cleansing properties will be considerably affected by the electrolytic impurities in H_2O . For example, with neutral or acid soap sols., the presence of large quantities of Ca or Ba salts or salts of trivalent metals will produce water-in-oil emulsions, which are very sticky and difficult to remove by H_2O . The pptn. of sols in emulsions, the coagulation of natural emulsions such as milk, and the effects of free alkalies and free fatty acids have been studied.

H. J. CREIGHTON

Flame as example of a stationary dispersoid system. P. P. VON VEIMARN. *Ann. école mines Oural* 1, Part 2, 5-6(1919).—A flame represents a "stationary" not "stable" dispersoid system because in a stable system the particles do not change, while in a flame they constantly disappear, but are constantly renewed. The deposition of soot is likened to the coagulation of colloidal flakes, both being due to a concn. of particles exceeding the concn. which corresponds to the stationary state. The luminosity of a flame is most probably a function of the degree of dispersion of the dispersoid part of the stationary system. Whether the max. of the former corresponds to the max. of the latter, expts. will decide.

H. M. GORDIN

Electrification of water and osmotic flow. JACQUES LOEB. *Science* 53, 77-84 (1921).—A presidential address. Work previously published (*C. A.* 14, 187) is presented. In addition L. has found that by treating this colloidion membrane with a protein coating and regulating the acidity he can reverse the effects previously described. Water can be made to diffuse through negatively charged, attracted, now, by the cations and repelled by anions. The attraction and repulsion bear the same relation to the valence of the ions previously described.

A. E. STRARN

Mobility of ions which are the same as those of the solvent. C. v. HEVESY. *Z. Elektrochem.* 27, 21-4(1921).—On the basis of Noyes' cond. measurements (cf. *C. A.* 2, 614, 2330), it is shown that the anomalous high mobility of the H^+ and OH^- ions disappears at high temps. and that the motion of the ions of H_2O follows the same laws as other ions. Comparison of the mobility of the H^+ ion and the H_2 mol. shows that the latter moves very rapidly in comparison with the "normal" ions, and only 1.5 times more slowly than the H^+ ion. The following values have been calcd. for the viscosity of water: at $218^\circ 0.001205$, and at $306^\circ 0.000927$ c. g. s. units. H. J. CREIGHTON

The dissolving and dissociating power of non-aqueous ionizing media in the presence of binary salts. PAUL WALDEN. Univ. Rostock. *Z. Elektrochem.* 27, 34-7 (1921); cf. *C. A.* 15, 202.—In satd. solns. at 25° in a number of non-aq. ionizing media, the binary electrolyte $N(CH_3)_4CNS$ has the same degree of dissociation $\alpha_1 = \alpha_2 = 0.380$; for the soly. of this salt at 25° the relation $\epsilon/\mu^{1/2} = 34$, where ϵ is the dielec. const. of different solvents and μ is the mol. soly. of the salt in the solvent. H. J. CREIGHTON

A modified hydrogen electrode. J. HUDIG AND W. STURM. *Chem. Weekblad* 16, 473-81 (1919).—In their measurements of the H-ion concn. of aq. soil exts. by means of the H electrode, the authors experienced difficulty in obtaining const. results for any one ext., even after filtration of the latter through an ultra-filter. While no explanation of the observed fluctuations in e. m. f. is suggested, it is found possible to obtain satisfactory constancy in the readings by the following modifications in the construction and use of the H electrode. The electrode consists of a Pt gauze cylinder platinized over a gold coating. The soil suspension is contained in a closed vessel, through the stopper of which pass the electrode, gas inlet and outlet tubes, electrolyte tube, and a stirring gear motor-driven through a mercury seal. A rapid stream of H is supplied both to the inner and to the outer surface of the gauze cylinder during the measurement, while soil and liquid are kept in intimate contact by vigorous stirring. J. C. S.

The viscosity of oils and other liquids as a function of the temperature. H. SCHWEDHELM. *Chem.-Ztg.* 45, 41-2 (1921).—Using data on Roumanian, Galician, and American mineral oils as measured by the Engler viscosimeter, S. proposes the equation $\eta/A = (\eta_0/A)^B (t_0 - t)^D$. Where η_0 is the absolute viscosity at the Celsius temp. t_0 , A and B are arbitrary constants. The maximum deviation of the calculated values from the observed is about 5%. The formula holds for non-lubricants such as hexane, benzene and ethyl alc. It leads to a limiting value for the viscosity ($\eta = A$), as the temp. increases, which is nearly the same (0.02 poises) for all lubricants, whether mineral oils or fatty oils; but the limiting value is of course much higher for the non-lubricants. Differences among the lubricants manifest themselves in variations in the exponent B . EUGENE C. BINGHAM

Influence of the solvent on the temperature coefficient of certain reactions. A test of the radiation hypothesis. HENRY E. COX. *J. Chem. Soc.* 119, 142-58 (1921); cf. *C. A.* 14, 2337.—The author's summary is: "The influence of 8 chem. dissimilar solvents upon the temp. coeffs. of the reaction of bromoacetophenone with aniline, and of 9 chem. similar solvents upon the reaction of sodium β -naphthoxide with EtI has been measured. The equation of Arrhenius for the effect of temp. does not require any relation between the velocity and temp. coeff., but the mathematical development of the radiation theory by Lewis and others requires that the temp. coeff. of the reaction in the several solvents shall be inversely proportional to the velocity in that solvent. These expts. have been designed to test this deduction of the radiation theory, and to throw some light on the role of the solvent in chem. kinetics by showing to what extent the solvent may be considered as a simple catalyst; and to what extent it has a constitutive effect dependent upon the chem. constitution of the solvent-solute complex. Temp. coeffs. of the refractive indexes of the solvents for the D-line have been measured, and the effect of this on the temp. coeff. of the velocity is considered; the effect of dissociation of the solute in the case of the reaction of sodium naphthoxide is also discussed. It is found that the temp. coeff. is inversely as the velocity in similar solvents for the reaction of bromoacetophenone, and for the reaction of sodium naphthoxide in those solvents in which the extent of ionization is similar; but that the relationship does not hold for dissimilar solvents, so that these cannot be regarded as simple catalysts, and the radiation theory does not apply in such cases. The radiation theory is, therefore, supported by these results when allowance is made for the special effects of the solvents.

The view is taken that reactions proceed by the formation of intermediate solvent-solute complexes, solvent action being a constitutive property by reason of the effect of the solvent on the constitution of the complex."

E. N. BUNTING

Ideal catalysis and the dislocation theory. J. BÖRSKERN. Univ. d'Agriculture, Wageningen. *Rec. trav. chim.* 39, 622-39(1920).—I. *The ideal catalyst.* Some years ago B. (C. A. 8, 3520) outlined his views on catalysis. This paper is a more extended account. Beginning with the Friedel-Crafts reaction in 1836 it was shown (*Rec. trav. chim.* 19, 19(1899); 20, 103(1900)) that $\text{RCOCl} + \text{AlCl}_3 \longrightarrow \text{RCOCl} \cdot \text{AlCl}_3$ and $\text{RCOCl} \cdot \text{AlCl}_3 + \text{C}_6\text{H}_6 \longrightarrow \text{RCOC}_6\text{H}_5 \cdot \text{AlCl}_3 + \text{HCl}$ represents the facts, and that 1 mol. AlCl_3 is required for each mol. RCOCl that reacts. The catalysis is not due to the formation of the addition product (*Rec. trav. chim.* 24, 6(1905)). B. found that the best catalysis occurs when AlCl_3 does not form such addition products, and that there is paralysis when it does (*Rec. trav. chim.* 23, 105(1904)). The catalysis of white P into red by AlCl_3 or I_2 is due not to the formation and decomn. of P_2I_4 but to the fact that I_2 can break P_4 into P_2 . But this decomn. does not give a satisfactory explanation of catalytic phenomena, because a complete splitting represents too strong an action for catalysis. This is why B. prefers as an explanation a *dislocating* action by the catalyst on the mols. actuated, a type of displacement of internal equil. by which the mols. are prepared for a more stable equil. (C. A. 4, 1434; 7, 1702). Because the intermediate-compd. theory is still encountered (Abel, C. A. 8, 597) B. repeats his views here (C. A. 5, 3190) showing it cannot explain the cause of catalytic action. Gattermann (*Die Praxis d. org. Chemikers* 14th. Ed., 253(1919)) explains the action of Fe on the bromination of C_6H_6 as due to the formation of FeBr_3 , reduction to FeBr_2 by C_6H_6 and reformation of FeBr_3 . But Al and Sb act similarly, although SbBr_2 and AlBr_2 are unknown. B. summarizes his introduction by saying that the catalyst ought to be in a state of dissociation (no addition complex) with the mols. activated, and that this equil. ought to be situated as far as possible toward the free mols. The best catalysts will be those in which this state of dissociation embraces an extensive interval of temp. and pressure in which its influence becomes neither too weak nor too strong. To discuss these ideas concretely B. uses material previously published by him. From an investigation (*Rec. trav. chim.* 32, 112 (1913)) of the equil. chloral \rightleftharpoons metachloral, B. concludes that H_2SO_4 and $\text{C}_6\text{H}_5\text{N}$ activate the reaction to the right because they exercise a chem. influence on the group $-\text{C}=\text{O}$, but that they approach the ideal catalysis only when the catalyst is present with the mols. activated in a state of equil. which is situated as far as possible from the side of the free mols. From an examn. of the decomn. of fatty acids in ketones and CO_2 B. concludes that BaO is not an ideal catalyst for this reaction. The formation of Et_2O and C_2H_4 by dehydration of EtOH (cf. B. in *Kochwasserstoffen*, I, 77-84) is discussed at length. It is concluded that in most cases the catalysts are far from ideal but are used to advantage in prepn. The catalysts for acetylation with Ac_2O (acids) or with AcCl (bases) are paralyzed by the formation of stable inactive derivs. This is not true to such an extent when $\text{C}_6\text{H}_5\text{N}$ is used. B. concludes that the ideal catalysis is never attained but it is approached if the conditions of the reaction have been chosen so that the catalyst forms chem. equils. with the combination activated which are displaced as far as possible toward complete scission, while none of the mols. in the system exercises paralyzing action on the catalyst. II. *The dislocation.* The above considerations aid in the selection of a catalyst but do not explain why a catalyst augments the velocity. For example $\text{C}_6\text{H}_5\text{N}$ ought to be a good catalyst for the acetylation of phenols with Ac_2O because this tertiary base can unite with 2 mols. with the formation of dissociable compds. which play the primary role in the acetylation. But in order to accelerate the reaction $\text{C}_6\text{H}_5\text{N}$ ought to satisfy a second condition: the interactions between catalyst and the 2 mols. ought to take place very rapidly and it is only if the

cause of this sudden action is given that we can speak of a definite explanation of catalysis. In using the general (but vague) formula of Nernst for the velocity of reaction $i = fe/r$ it is necessary that e and r should simultaneously approach zero (f_{max} for $\lim, e = 0$)/($\lim, r = D$). The purely kinetic theory cannot give a satisfactory explanation because it is necessary to det. why the collisions of mols. with the catalysts, in spite of their small no., and the small differences in free energy, may have so large an effect. Guye (*J. chim. phys.* 15, 262(1917)) has applied the law of probability to this question but this explanation is of value only if one knows why the activator "catches" the mols. activated. Unfortunately it has nothing to say about the character of the catalyst. It does not explain why H_2 and O_2 may not both serve as catalysts in the formation of H_2O . To explain the sudden action of the catalyst it is necessary to consider the character of the catalyst with respect to the combination activated. The mols. activated are never exclusively monatomic substances; they always act on mols. with 2 or more atoms. Polyatomic mols. may be considered as closed systems and so act slowly or not at all. The essential action of a catalyst is to open these systems. Accordingly the catalyst ought to be an open system and able to transmit this quality to the combinations which it is to activate. The most powerful catalysts should be monatomic mols. (metals) and unsatd. mols. or those having residual valences. This type of mols. can cause intense perturbations in the internal equil. of closed mols. This disturbing action B. has called "dislocation." Within the lapse of the very short time of a collision between catalyst and mol. the field of internal forces (orbits of the electrons) will be displaced in such a way that these mols. act immediately. A substance may exercise such an influence without being an ideal catalyst, but it is then paralyzed during the reaction (Baumann-Schotten and Friedel-Crafts reaction). The changes affected by the presence of the catalyst will need to be examd. by elec. methods or by photochem. research. The photocatalytic phenomena will give the information desired because in these cases an indifferent substance is changed by an exterior and measurable action into a catalyst and this transformation takes place immediately at the moment when the substance is struck by the active rays. In this connection B. reviews the results of Cohen and B. (*C. A.* 10, 3068) and E. Baur (*C. A.* 13, 282), from which it seems probable that catalysts act like luminous rays. This would require an exchange of energy but this quantity of energy may be very small in comparison with the quantities of matter put into action. The relation between these quantities has always been a measure of the ideality of the catalysis. The more one is able to transform with a given quantity of luminous energy or of a catalyst the more one approaches the ideal photo- or "materio"-catalysis. These small transfers of energy B. calls the "dislocations."

E. J. WITZEMANN

Catalytic decomposition of hydrogen peroxide by ferric salts. VAN L. BOHNSON. *J. Phys. Chem.* 25, 19-54(1921); cf. *C. A.* 15, 975.—Ferric salts accelerate the decompn. of H_2O_2 to a greater degree than NaI in equiv. concn. For dil. solns. of $FeCl_3$ and $Fe(NO_3)_3$ the velocity is proportional to the concn. $Fe_2(SO_4)_3$ is less effective than $FeCl_3$ and $Fe(NO_3)_3$. The equations representing the probable modes of catalysis are as follows: (1) $2FeCl_3 + 3H_2O_2 + 2H_2O \rightleftharpoons 2H_2FeO_4 + 6HCl$, (2) $2H_2FeO_4 + 3H_2O_2 \rightarrow 2Fe(OH)_2 + 2H_2O + 3O_2$, (3) $2Fe(OH)_2 + 6HCl \rightleftharpoons 2FeCl_3 + 6H_2O$, in which (2) is the measurable reaction. Consts. were obtained for a monomol. reaction. The specific reaction velocity decreases as the reaction proceeds, owing to hydrolysis of the catalyst. Such products of hydrolysis as colloidal $Fe(OH)_3$ or basic salts have no catalytic effect. The addition of free acid retards the reaction, apparently by reducing the concn. of the intermediate product. Salts having an ion in common with the catalyst retard the decompn. by decreasing the dissociation of the catalyst. The slightly dissociated $HgCl_2$ has a very small influence. The accelerating effect of a mixt. of $Fe_2(SO_4)_3$ with

FeCl_3 or $\text{Fe}(\text{NO}_3)_3$ is not as great as the sum of their separate effects. CuSO_4 greatly hastens the $\text{Fe}_2(\text{SO}_4)_3$ catalysis. Alcohol, glycerol, sugar, urea and acetanilide act as anti-catalysts in the presence of ferric salts.

C. C. VAN VOORHIS

.. Dissociation pressures of iron nitrides. A. A. NOYES AND L. B. SMITH. *J. Am. Chem. Soc.* 43, 475-81 (1921).—The equil. conditions of the reaction between Fe , NH_3 , solid iron nitrides, and H at 460° are detd. The equil. const. given by the expression $(p_{\text{NH}_3})^3/(p_{\text{H}_2})^3$ was found to vary with the proportion of N present in the solid phase. Thus with increasing nitrogen content this expression remained const. at the value 1.0 till the atomic ratio $\text{N}:\text{Fe}$ became 1:9; later increased rapidly, namely, to 5.2 for $\text{N}:\text{Fe} = 1:7.7$ and to 30 for $\text{N}:\text{Fe} = 1:4.9$; and finally assumed the much smaller value 2.1 for $\text{N}:\text{Fe} = 1:2.6$. These results indicate the formation: first, of a nitride of small N content, perhaps Fe_3N ; then, either of a metastable nitride, such as Fe_2N in solid soln. with the first one, or of 2 sep. metastable nitrides, such as Fe_2N and Fe_3N as sep. solid phases; and, finally, of a stable nitride, probably the well known Fe_3N . By combining this equil. const. with the const. $(p_{\text{NH}_3})^2/p_{\text{H}_2}(p_{\text{H}})^2$ for the formation of ammonia, the dissociation pressures p_{H_2} of the nitrides in the various solid phases were computed to be 20,000, 102,000, 590,000 and 41,000 atm., resp. JAMES M. BELL

The notion of affinity. A. KOREVAAR. *Chem. Weekblad* 18, 37-9 (1921).—The two uses in the chem. literature of the word affinity are discussed: first, the classical use of the word as synonymous with the chem. force between atoms; and second the modern thermodynamical notion, according to which it is defined as the max. work that can be obtained from the given reaction. The connection between chem. force and max. work, and between max. work and the equil. const. is pointed out, but in spite of the general acceptance of the thermodynamical definition of affinity, K. deprecates this use of the word. He presents arguments to the effect that less confusion would result if max. work were called max. work, and affinity were reserved to express something akin to its original connotation. Thus, according to K., the driving force of a chem. reaction would be described as being proportional to the product of the concns. of the reacting substances and the affinity (or affinity coeff.).

L. H. ADAMS

Double decompositions of salts and the phase rule. ETIENNE RENGADE. *Compt. rend.* 172, 60-2 (1921).—The equil. $\text{NaNO}_3 + \text{NH}_4\text{Cl} \rightleftharpoons \text{NH}_4\text{NO}_3 + \text{NaCl}$ in H_2O is discussed. Whether or not a third solid is formed, when two salts are put in contact with H_2O depends upon the soly. of the products, and in either case there is no contradiction of the phase rule.

E. N. BUNTING

The dependence of the heat of vaporization of water on the temperature. H. v. STEINWEHR. *Z. Physik* 1, 333-6 (1920).—A purely thermodynamic relation between the latent heat, temp. and the sp. heats is derived, which agrees with the Reichsanstalt values for water from 40° to 180° within 0.5 per mille, and yields the equation: $(r/T_2) - (1/T)(dr/dT) + (ds/dT_2) = d(h - s)/dT$ for the heat of vaporization, r , of all substances where h — the difference of the sp. heats of liquid and vapor is a linear function of the temp.

W. P. WHITE

Solubility. VI. Thermodynamic relation between solubility and internal pressure. J. H. HILDEBRAND. *J. Am. Chem. Soc.* 43, 500-7 (1921); cf. C. A. 15, 6.—The author's summary is: It has been shown thermodynamically that only such liquids as have identical values of $(\delta P/\delta T)_v$ are capable of yielding solutions obeying Raoult's law under all conditions, i. e., at all temperatures, pressures and compositions. It is proposed to define internal pressure as $T(\delta P/\delta T)_v$, one of the terms of the thermodynamic equation of state. Illustrative values are given for the internal pressures of certain liquids calculated in this way. Since the internal pressure of a solution of non-polar liquids is probably a linear function of the composition expressed in terms of mol. fraction, it is probable that the difference between the internal pressures of the two pure liquids would

determine, at least to a considerable extent, the deviation of the solution from Raoult's law. This is essentially the theory heretofore outlined and supported by abundant experimental data. The criteria previously used for estimating relative values of internal pressure are shown to be in substantial accord with the thermodynamic definition of internal pressure here used, although it is theoretically preferable to use surface energy in place of surface tension.

JAMES M. BELL

Equilibrium of the four-component system: sodium sulfate, sodium bicarbonate, ammonium sulfate, ammonium bicarbonate and water. II. KYOSUKU NISHIZAWA. *J. Chem. Ind. (Japan)* 23, 1015-26 (1920).—In previous article (*C. A.* 14, 2741), N. reported on the equil. of the same component system, basing some of his expts. for decompn. pressure of NH_4HCO_3 on the data obtained by Dibbitts (cf. *J. prakt. Chem.* 1874, 417). Since N.'s own detns. on the decompn. pressure of the salt for 5-40° (cf. *C. A.* 15, 1237), vary somewhat from those of D., N repeated some of his earlier expts. on equil. of this reciprocal salt pair at 30° and 40° under corresponding decompn. pressure of the satd. soln. of NH_4HCO_3 . The results are plotted in 5 curves, the summary of which is as follows.

Temp. Point Solid Phases.		Composition of the solution in g. mol. per 1000 g. mol. H_2O Na_2SO_4 $(\text{NH}_4)_2\text{SO}_4$ NH_4HCO_3 NaHCO_3			
30°	a ₁ $\text{Na}_2\text{SO}_4 \cdot 10\text{H}_2\text{O}$	52.01
30°	b ₁ $(\text{NH}_4)_2\text{SO}_4$...	106.20
30°	c ₁ NH_4HCO_3	59.57	...
30°	d ₁ NaHCO_3	23.61
30°	A ₁ $\text{Na}_2\text{SO}_4 \cdot 10\text{H}_2\text{O}; \text{NaHCO}_3$	48.84	8.55
30°	B' $\text{Na}_2\text{SO}_4 \cdot 10\text{H}_2\text{O}; \text{Na}_2\text{SO}_4$	61.33	13.75
30°	B ₁ $\text{Na}_2\text{SO}_4; \text{Na}_2\text{SO}_4 \cdot (\text{NH}_4)_2\text{SO}_4 \cdot 4\text{H}_2\text{O}$	55.30	33.18
30°	C ₁ $\text{Na}_2\text{SO}_4 \cdot (\text{NH}_4)_2\text{SO}_4 \cdot 4\text{H}_2\text{O}; (\text{NH}_4)_2\text{SO}_4$	20.21	98.73
30°	D ₁ $(\text{NH}_4)_2\text{SO}_4; \text{NH}_4\text{HCO}_3$...	99.27	24.60	...
30°	E ₁ $\text{NH}_4\text{HCO}_3; \text{NaHCO}_3$	37.96	12.38
30°	F' $\text{Na}_2\text{SO}_4 \cdot 10\text{H}_2\text{O}; \text{Na}_2\text{SO}_4; \text{NaHCO}_3$	57.25	14.58	7.09
30°	F ₁ $\text{Na}_2\text{SO}_4; \text{Na}_2\text{SO}_4 \cdot (\text{NH}_4)_2\text{SO}_4 \cdot 4\text{H}_2\text{O}; \text{NaHCO}_3$	55.03	31.83	7.85
30°	G ₁ $\text{Na}_2\text{SO}_4 \cdot (\text{NH}_4)_2\text{SO}_4 \cdot 4\text{H}_2\text{O}; \text{NaHCO}_3; \text{NH}_4\text{HCO}_3$	11.27	87.04	27.56
30°	H ₁ $\text{Na}_2\text{SO}_4 \cdot (\text{NH}_4)_2\text{SO}_4 \cdot 4\text{H}_2\text{O}; \text{NH}_4\text{HCO}_3; (\text{NH}_4)_2\text{SO}_4$	8.68	104.06	24.66
40°	a ₂ Na_2SO_4	61.01
40°	b ₂ $(\text{NH}_4)_2\text{SO}_4$...	110.6
40°	c ₂ NH_4HCO_3	75.77	...
40°	d ₂ NaHCO_3	26.92
40°	A ₂ $\text{Na}_2\text{SO}_4; \text{NaHCO}_3$	57.14	9.45
40°	B ₂ $\text{Na}_2\text{SO}_4; \text{Na}_2\text{SO}_4 \cdot (\text{NH}_4)_2\text{SO}_4 \cdot 4\text{H}_2\text{O}$	51.3	47.3
40°	C ₂ $\text{Na}_2\text{SO}_4 \cdot (\text{NH}_4)_2\text{SO}_4 \cdot 4\text{H}_2\text{O}; (\text{NH}_4)_2\text{SO}_4$	25.0	102.4
40°	D ₂ $\text{NH}_4\text{HCO}_3; (\text{NH}_4)_2\text{SO}_4$...	100.9	34.0	...
40°	E ₂ $\text{NH}_4\text{HCO}_3; \text{NaHCO}_3$	70.83	15.84
40°	F ₂ $\text{Na}_2\text{SO}_4; \text{Na}_2\text{SO}_4 \cdot (\text{NH}_4)_2\text{SO}_4 \cdot 4\text{H}_2\text{O}; \text{NaHCO}_3$	49.33	45.41	11.26
40°	G ₂ $\text{Na}_2\text{SO}_4 \cdot (\text{NH}_4)_2\text{SO}_4 \cdot 4\text{H}_2\text{O}; \text{NaHCO}_3; \text{NH}_4\text{HCO}_3$	10.03	109.1	34.59
40°	H ₂ $\text{Na}_2\text{SO}_4 \cdot (\text{NH}_4)_2\text{SO}_4 \cdot 4\text{H}_2\text{O}; \text{NH}_4\text{HCO}_3; (\text{NH}_4)_2\text{SO}_4$	9.79	109.2	35.48

These results were applied to the ammonia-soda process. N.'s new process is to use Na_2SO_4 as raw material and combine the general ammonia-soda process with cyanamide process for manuf. of $(\text{NH}_4)_2\text{SO}_4$.

S. T.

Conditions at copper anodes in solutions of alkali hydroxides. FR. JIRSA. Prague. *Z. Elektrochem.* 27, 30-4 (1921).—See *C. A.* 15, 344. H. JERMAIN CRIGHTON

The magnetic molecular field. RICHARD GANS. La Plata. *Ann. Physik* 63, 382-96(1921).—G. assumes that the elementary magnetic particle of paramagnetic substances is acted on by an outside magnetic force, and also by a magnetic force due to neighboring elementary magnets. He shows mathematically that at abs. zero, whether it is assumed that the resultant force is ∞ (saturation) or zero (disorder) the curves for $M/M\infty$ (specific magnetization) plotted against A_0 (the most probable resultant field) are the same within a fraction of a percent. The formula $M/M\infty = \phi(r) - \{\phi(r) + \phi'(r)\}/2r^2$ (where $r = K/A^\circ$ and $\phi(r)$ are tabulated for the sp. magnetization), therefore, holds, and it is justifiable to assume that at zero abs. all directions of the mol. magnetic field are equally likely. Cf. C. A., 5, 1868. Presumably the same formula holds approx. for higher temps. F. R. B.

Graphic table of air densities. WALTER BLOCK. *Z. tech. Physik* 1, 278-80 (1920).—An easily prepd. chart for finding air densities is described. It covers the pressure range 720-775 mm., the temp. range 15° to 27° , and humidities from 30 to 90%.

D. MACRAE

Fundamentals of the theory of color measurement. W. OSTWALD. *Z. tech. Physik* 1, 173-5, 261-71(1920); cf. C. A. 15, 739.—A discussion of the theory and use of Ostwald's chrometer.

D. MACRAE

Preparation of small pieces for microscopic examination. HENRY S. RAWDON. *Chem. Met. Eng.* 24, 475-6(1921).—Specimens too small for convenient handling are coated with a heavy deposit of electrolytic Cu, mounted in a matrix such as tin solder or other alloy, and then a section through the resulting duplex specimen is cut and polished.

S. D. KIRKPATRICK

Catalysis in industrial chemistry (RIDEAL) 13. Atomic structure and chemical properties (KOHLEWILER) 3.

LEWIS, WILLIAM C. McC.: A System of Physical Chemistry. Three Vols. Third Ed. London: Longmans, Green & Co. 453 pp. 15 s. For review see *Pharm. J.* 106, 112(1921).

MACDOUGALL, FRANK H.: Thermodynamics and Chemistry. New York: John Wiley & Sons. 391 pp. \$5.50 net.

3—SUBATOMIC PHENOMENA AND RADIOCHEMISTRY

GERALD L. WENDT

The constitution of atoms. ORME MASSON. Univ. Melbourne. *Phil. Mag.* [6] 41, 281-6(1921).—M. suggests that the elementary positive particle of charge +1 and mass 1 should be termed "baron" to suggest mass as its most distinguishing characteristic. In a foot-note Rutherford states that Section A of the Brit. Assoc. at the recent meeting at Cardiff, approved the term "proton" as being more suitable. M proposes a simple system of notation and formulation for the nuclear reactions involving electrons and "protons," which is similar to ordinary chemical formulation. For example the two modes of disruption of the N atom, which Rutherford has found to result in the expulsion either of a He atom of mass 3 or of a "proton" would be expressed as follows: $[(p_e)_1]e_1 = [(p_e)_1(p_e)]e_1 + (p_e \rightarrow)$ and $[(p_e)_1]e_1 = [(p_e)_1(p_e)]e_1 + p \rightarrow$, in which p is a proton, e an electron, subscripts mean multipliers and letters, parentheses and brackets written in juxtaposition signify addition, as in chemical formulas, not multiplication. Some anomalous characteristics of the H atom are pointed out and some relations among the pure elements and the highest members of isotopic groups.

S. C. LIND.

Atomic structure and chemical properties. E. KOHLWEILER. *Physik. Z.* 21, 543-9(1920); cf. *C. A.* 14, 2747, 3188.—Further arguments in favor of the view that chem. processes have their origin mainly in the nucleus of the atom, although they may be secondarily affected by the external electrons. If the electrons were the only factors in chem. reactions then an α -particle ought to be bivalent, whereas it has an affinity only for electrons. K. emphasizes specially the fact that ions occur in canal rays, with positive charges which do not correspond at all to chem. valencies. Thus Hg can lose 8 electrons to form an ion with 8 positive charges, but it is never octavalent. Numerous physical properties vary with the number of external electrons in a given atom, but not the chem. properties. Thus there are colorless diamagnetic cuprous salts and blue paramagnetic cupric salts, but in both cases the same element, Cu, exists. "Nuclear structure and charge are the fundamental data of the chem. elements." S. DUSHMAN

Constitution of matter and electricity. A. N. SRIVASTRA. *Chem. News* 122, 37(1921).—Matter is condensed. No evidence or theory is given. L. D. R.

The storing of light. J. FREDERICK CORRIGAN. *Chem. News* 122, 25-7(1921).—An historical review of phosphorescence of inorg. substances with no discussion of the modern theories of luminescence. L. D. R.

The isotopism of mesothorium and radium and the separation of these elements from barium. RALPH K. STRONG. *J. Am. Chem. Soc.* 43, 440-52(1921).—1100 g. of BaCl₂ containing 11 mg. of MesoTh and 3 mg. of Ra were prepd. from monazite residues. Concns. were made by the McCoy hydroxide method and by the bromide method. All concns. showed the same MesoTh/Ra ratio. In this work a large number of transformations and crystns. are made, but the ratio does not change. This work furnishes further evidence that MesoTh and Ra are isotopic. L. D. ROBERTS

Collision of alpha particles with hydrogen atoms. E. RUTHERFORD. Univ. Cambridge. *Phil. Mag.* 41, 307-8(1921).—A note describing improvements in the method of counting scintillations, consisting in using holoscopic lenses of wide aperture and suitable eye-pieces. The detn. of the number of H atoms ejected from the atoms of different elements by α -particles of various speeds is being continued in the Cavendish Lab., both by the scintillation and by an elec. balance method. R. also points out that the use of $\cos \theta$ as the correcting factor in calcg. the emergent range of H atoms scattered at an angle θ is only a rough approximation. The av. value is a complete function of θ which can be readily calcd. S. C. LIND

Thomson effect and thermal conduction in metals. ROWIN H. HALL. *Proc. Nat. Acad. Sci.* 6, 613-21(1920).—H. revises some of the equations set up in a previous paper (*C. A.* 14, 3352) in which he deduces the various constns. for his theory of dual elec. conduction from the exptl. values found by Bridgman for the Thomson effect. This revision involves a change in the equation No. 11 of the previous paper and corresponding alterations are made in other of the resulting equations. This modified theory yields temp. coeffs. of cond. more nearly in agreement with exptl. facts than did the previous theory. It still remains to adapt the values obtained to the Peltier effect; the results obtained in this connection will form the basis of another paper. L. B. LOEB

Possible magnetic polarity of free electrons. ARTHUR H. COMPTON. Cambridge Univ. *Phil. Mag.* 41, 279-81(1921).—Some unpublished photographs by C. T. R. Wilson show that the paths of β and secondary cathode rays excited in air by X-rays usually terminate in converging helices, which may be either right or left-handed. The axial orientation is nearly random. The spiral form of path could be accounted for by motion in a magnetic field, and the chance orientation shows that the axes are not detd. by an external fixed field. A β -particle acting as a magnetic doublet as well as an elec. charge would be capable of producing a magnetic field if the medium through which it

passes is susceptible to magnetization. C. discusses the effect according to this theory and deduces an equation for the intensity of the magnetic field which he finds would be about 3000 gauss; this is of the right order to account for the observed curvature of path. Other important deductions can be made from the magnetic doublet theory.

S. C. LIND

Measurement of the (atmospheric) ionization and ionic mobilities in balloon ascensions. ALBERT WIGAND. *Physik. Z.* 22, 36-46(1921).—Measurements of the atm. ionization and the mobilities of the atm. ions at different altitudes were made during 4 balloon ascensions, and 2 airplane trips. Altitudes of 4.1 km. were attained in the former, and 5.2 km. in the latter case. Great pains were taken to note the meteorological conditions during the measurements. The number of ions increased with the altitude. This increase was not const., for in the first $1\frac{1}{2}$ to 3 km., where clouds, dust, and haze abound, the number of ions remained const. or even decreased with increasing altitudes. Above this height the number of ions increased to several times the number found at the surface. [The author makes no mention of any corrections for a possible increase in elec. leakage of his app. due to the decrease in temp. in the higher regions, an effect which Kunsman recently showed to be of importance (*C. A.* 15, 13). Such an effect could have accounted for the apparent increase in the number of ions in the upper regions.—Abstractor.] The initial constancy or even decrease of the ionization found below 3 km. is explained by the fact that as the earth is left the effect of the radioactive substances in its surface becomes less, and also by the fact that in the regions where dust and water vapor abound the number of ions is reduced by the increased rate of recombination due to these agents. The number of ions was found to vary with the weather conditions, though apparently in no regular manner. At the higher altitudes in general the positive charges were more numerous than the negative charges, except in the case of thunderstorm conditions, when the negative charges were more numerous than the positive. There is some doubt as to these latter results owing to the possibility that the charge on the balloon exerted a selective action on the charge carriers available, though attempts were made to reduce such an effect. The measurements on the ionization before and after sundown showed no change in the number of ions found. This definitely shows that the ultraviolet rays of the sunlight at these altitudes do not cause an appreciable ionization. The mobilities of the ions when reduced to atmospheric pressures increase with increasing altitudes from 0 to 2 km., to about double their value at the earth's surface. Thereafter there does not seem to be any further change in the mobility constant. This was considered to be due to the action of the H_2O vapor and the dust at the lower altitudes in decreasing the average values of the mobility, for it was observed that with decreases in the humidity the values of the mobility increased where the mobilities were not too small to begin with. The absolute values of these mobilities, however, might well be in error. L. B. LOEB

The formation of negative ions in air. L. B. LOEB. *Phys. Rev.* 17, 89-115(1921); cf. *C. A.* 14, 3582.—The abnormal increase of the mobility const. for negative carriers in air at pressures below 100 mm. with decreasing pressure has been ascribed by both Wellich and J. J. Thomson to the nature of the process of attachment of the electron to neutral mols. to form the ions. Both Wellich and Thomson have proposed theories as to the nature of this process, which theories are, however, mutually exclusive. L. undertook a study of the behavior of the photo-electrons in attaching to mols. in air at pressures in the neighborhood of 100 mm., using the mobility curves obtained with the Rutherford alternating-current method of mobility measurement. An equation was deduced on the basis of the Thomson theory which permitted the type of curves to be expected on the Thomson theory to be computed for the exptl. conditions used by the author in his expts. These theoretical equations could be applied as soon as a certain

const., n , had been detd. from expt. The Thomson theory postulates that an electron may attach to a mol. on the av. only after n collisions; where n is a const. of the gas mol. present. Such a theory would be expected if an electron were able to attach to a mol. only when it struck a certain region in the mol. This const. n was found experimentally to be about 250,000 in air, assuming certain values for the electronic mobility and mean free path. Putting this value of n into the equation for the Thomson theory a good qual. agreement was obtained between the observed and computed curves. Closer agreement is not possible until the value of the electronic mobility and its variation with pressure and voltage become accurately known. The agreement is, however, close enough to warrant one in adopting the Thomson theory. A careful repetition of the expts. of Wellisch which lead him to his theory of ion formation, as opposed to the Thomson theory, show that the Wellisch theory resulted from a misinterpretation by Wellisch of some of his results. Actually the Wellisch results are in excellent accord with the Thomson theory. The conclusion is that the electron can attach to a mol. to form an ion in air on the av. only after 250,000 impacts if the values for the electronic mobilities assumed are correct. [Recent measurements of the electron mobility show it to be much higher (about 10,000 cm./sec. per volt/cm. compared to 200 cm./sec. per volt/cm.), than the values found by previous observers and used in this calcn. This reduces the value of n for O_2 to about 1000 instead of the 50,000 used above.—ABSTR.]. Expts. in pure N_2 and H_2 (C. A. 14, 3582) show that the electron does not attach to these mols. to form negative ions. Expts. in O_2 show that the value of n for O_2 is about 50,000. So that it appears to be the O_2 mol. in air to which the electron attaches. This process of attachment does not seem to be a function of the energy of the electron. It depends, therefore, either on the presence of a certain active type of mol. in the gas in small quantities to which electron can attach, or on the region of the atom struck.

L. B. LOEB

Ionization and excitation of radiation by electron impact in helium. FREDERICK S. GOUCHER. *Proc. Phys. Soc. (London)* 33, I, 13-29(1920).—The measurements were made on the critical potentials of He by the method of Davis and Goucher. The abs. values of the critical potentials were detd. in these expts. the value of the ionizing potential of Hg vapor being used as standard. Assuming an ionizing potential of Hg of 10.4 v. Goucher obtained a radiation potential in He at 20.0 v. and an ionizing potential in He at 26 v., in good agreement with the values of Horton and Davies. Some ionization was observed at the lower radiating potential. This was ascribed to the presence of some more easily ionized impurity. It might also have been due to an electronic impact on a radiating atom.

L. B. LOEB

Ionization and dissociation potentials in hydrogen. THEA KRÜGER. *Ann. Physik* 64, 288-304(1921).—In order accurately to det. the dissociation potential of the H mol., and properly to explain the ionization and resonance phenomena in H gas K. made a critical exptl. study of the ionization and resonance potentials in H using two of the methods used by Franck and Knipping (C. A. 14, 2126) and also the method of Bergen, Davis and Goucher. The absolute values of the potentials observed were detd. by mixing He with the H in some expts., and detg. the values of the H potentials from the location of the breaks due to resonance and ionization in He, the values for which have been accurately detd. by Frank and Knipping. The results obtained yield: At 11.5 ± 0.7 v., weak ionization and weak radiation; at 13.6 ± 0.7 v., strong radiation; at 17.1 ± 0.25 v., strong ionization; at 30.4 ± 0.5 v., strong ionization. K. next considers what changes may occur in H when bombarded by electrons of different velocities in order to explain these phenomena. She assumes the following processes: (1) If the molecular, H_2^+ ions can exist (an assumption which is unlikely on the Bohr hypothesis), these carriers would be the first type to be formed when the electrons ac-

quired the requisite ionizing energy. (2) If the mol. absorbs energy equal to the sum of the resonance potential (R) and the energy (D) required for dissociation, there will be formed a neutral atom of H and a radiating atom of H. (3) If the mol. absorbs energy equal to the ionization energy of the atom (I) plus the dissociation energy (D) then there will be formed a positively charged H^+ atom, and a neutral H atom. (4) If the mol. absorbs the energy ($I + R + D$) in an electronic encounter, one ion and one radiating atom are obtained. (5) If the energy ($D + 2R$) is absorbed 2 radiating atoms are obtained. (6) If the energy ($D + 2I$) is absorbed there are formed 2 positively charged H^+ atoms. K. attributes the 17.1 v. effect to an action of the type (3) above on the basis of the curves obtained in her expts. The 30.4 v. ionization is ascribed to case (6) above. From these she obtains 2 equations from which (D) may be computed. A weighted mean yields (D) as being equal to 3.53 ± 0.3 v. This potential corresponds to an energy of 81,300 cal. for the energy of dissociation, which is, within the limits of expl. error, equal to the Langmuir value of 84,000 cal. This value is not in agreement with the value predicted by the Bohr theory. The radiation at 13.6 v. is ascribed to the second type of event, and by calc. the value of (R) from the value of the frequency of the first absorption line in the H_2 absorption spectrum she gets (D) to be 3.5 v. She shows experimentally that one cannot cause dissociation of the H_2 mol. by electron impacts at 3.5 v., the dissociation potential. This was to be expected, for electron impacts, owing to small mass of the electron, are unable to impart enough energy to the atom of the mol. struck to cause dissociation. Dissociation of the H_2 mol. by impact then can only occur when the "cementing" electron is struck by an electron which has an energy equal to the sum of the dissociation energy and the radiating or ionizing energy. The 11-volt phenomenon she ascribes to a possible ionization produced by the positive H_2^+ mols. because of the dependance of this phenomenon on pressure. These results are in good accord with the results of spectroscopic analysis of different types of discharge.

L. B. LOEB

Electric discharge in hydrogen. D. N. MALLIK. *Phil. Mag.* 41, 3004-7(1921).—Certain anomalies exhibited by H with reference to the passage of electricity through it are pointed out. The failure to produce rotation effects in H in discharge tubes under conditions where they can be readily produced in air was regarded by M. as belonging to the same class of anomalies. Further examn. of the subject reveals, however, that the differences would be expected from the much lower density of H, and that the voltage necessary to produce rotation effects is much higher than for air.

S. C. L.

The theory of the high-vacuum discharge. GEORGE JAFFE. *Ann. Physik* 63, 145-74(1920).—For extremely high vacua, Langmuir (*C. A.* 8, 1230) and Child have developed the equations for the limitations of electron current by space charge. J. investigates mathematically the effect of slight traces of positive ionization on the space charge current. In the first part of the paper he deals with the case of plane electrodes, and finds that even under poor vacuum conditions a $3/2$ power law holds valid, but the actual current for any given voltage is greater than that obtained in good vacuum, the deviation increasing with pressure. The effect of initial velocities is also discussed. The second part of the paper deals with the effect of positive ions in the case of a filamentary cathode in the axis of a cylindrical anode. The correction term is found to be not in very good agreement with observed results. J. also discusses Lilienfeld's observations (*C. A.* 7, 3448) on conduction in long tubes and questions the latter's conclusion that the current-voltage characteristic is independent of the diameter of the discharge tube.

SAUL DUSHMAN

The theory of the high-vacuum discharge; comment on Mr. G. Jaffe's preceding work. J. E. LILIENFELD. *Ann. Physik* 63, 175-8(1920).—Lilienfeld defends his former statements (*C. A.* 4, 2765; 7, 3448; 9, 17; 14, 3017). See criticism of Lang-

muir (C. A. 8, 1230). Jaffe's calcs. (cf. preceding abstract) confirm his observations and agree with his empirical formula. Lilienfeld points out, however, that Jaffe's theory is not in agreement with the fact that the anode temp. is independent of the anode distance. Lilienfeld suggests again that positive electricity may be independent of ionization by collision.

FARRINGTON DANIELS

Density, dielectric constants, and refraction of solid salts. ADOLF HEYDWEILLER. Rostock. *Z. Physik* 3, 308-17(1920).—Baumann (*Diss. Rostock 1914*) has measured the dielec. consts. and ds. of 27 salts in finely powdered form, in which the d. is less than in the compact form. H. shows that these measurements agree with the Wiener formula for the dielec. const. as a function of d. provided Stoecker's values (C. A. 14, 3563) for the form number are used. This form number replaces the 2 in the Lorenz-Lorentz formula and should be the same for all substances. Three salts were measured with and without water of crystn.; the difference in the elec. refraction per mol. of H_2O is const., the refraction being calcd. from Wiener's formula, $R = (M/d)[(e-1)/(e+4)]$ (M = mol. wt., d = density, and e = dielec. const.). Also the optical index of refraction is shown to be very nearly equal to $1/2$ the long-wave elec. refraction, indicating that in the visible region the ultra-violet (electronic) and infra-red (ionic) vibrational properties take about equal part.

F. C. HOYT

Spectroscopic observations on X-Rays. E. WAGNER. *Physik. Z.* 21, 621-6(1920).—Using the method previously described (C. A. 13, 3072) except for an improved method of measuring voltages by the current through a standard high resistance, W. obtains as a mean value for h $6.53 \pm 1 \times 10^{-27}$ erg. sec. Within the limits of error the high frequency limit of the radiation at 90° and 150° with the cathode beam is the same. At these 2 angles there is a difference in the energy distribution in the spectrum, and in the sense of a Doppler effect at intermediate frequencies which vanishes at long wave lengths and at the high frequency limit. Measurements at other azimuths are to follow.

F. C. HOYT

Intensities of X-Rays of the L-series. III. Critical potentials of the platinum and tungsten lines. FRANK C. HOYT. *Proc. Nat. Acad. Sci.* 6, 639-44(1920).—Const. voltage photographs of the L-radiation from W and Pt reflected from the surface of a large stationary calcite crystal are used further to classify the spectral lines according to their critical potentials. (Cf. Webster, C. A. 14, 3583.) The classification at present is; L_1 $\alpha_1, \alpha_2, \beta_2, \beta_3, \beta_4, \beta_5, \beta_6, \beta_7, L_2$ $\gamma, \beta_1, \gamma_1$ and L_3 $\beta_1, \beta_2, \gamma_2$. This still leaves as undecided γ_2 and γ_3 .

F. C. HOYT

New X-Ray tube for Debye photographs. ASSAR HADDING. *Lund. Z. Physik* 3, 369-71(1920).—H. describes a small metal tube in which the anticathode is only 1 cm. from the window. At 37 kv. it will pass 20 ma.

F. C. HOYT

Recent advances in science—astronomy. H. SPENCER-JONES. Greenwich Observatory. *Sci. Progress* 15, 356-62(1921).—Includes a summary of recent work on the extension of the ultra-violet spectrum.

JOSEPH S. HEPBURN

Some special questions in the theory of band spectra. W. LENZ. *Physik. Z.* 21, 691-4(1920).—L. first gives a brief summary, with full references, of the recent application of the quantum theory to band spectra. [A complete account of this is given in Sommerfeld's "Atombau," 2nd ed., pp. 550-66.—ABSTR.] The theory is then shown to apply with particular clearness to the fluorescent spectrum of I vapor, as analyzed by Wood (C. A. 12, 1148). It is shown that the resonance doublet is due to the two changes of rotational energy of the mol. alone permitted by the selective principle. The entire series of doublets produced by a single exciting line correspond to the same rotation transitions, but to the various possible vibration conditions of the atoms of the mol. Collisions, augmented by greater vapor d. or a foreign gas, allow all possible quant. values of rotational energy, and so cause the complete resonance

spectrum. From Wood's numerical data the moment of inertia of the I mol. is computed as about 2×10^{-42} , corresponding to a sepn. of the at. nuclei of 1.4×10^{-8} cm. From the spectral relations the fundamental at. vibration frequency is computed as 6.4×10^{12} , indicating a sp. heat of 6.90, as compared to the exptly. detd. value 6.86. A method is indicated for detg. the origin of various bands from a knowledge of their structure. The article concludes with some general remarks concerning the theoretically expected thermal influence on the intensity distribution in band spectra, with a possibility of thus detg. stellar temps.

R. T. BIRGE

Influence of an electric field on the fine-structure of hydrogen lines. H. A. KRAMERS. Kopenhagen. *Z. Physik* 3, 199-223(1920).—K. gives a method for calcg. the wave lengths of the components into which an elec. field splits the Balmer series lines of H or He. The results, which take account of the variation of the electron mass with velocity, hold for all values of the elec. field strength, and so even when the displacement is small compared to the original "relativity fine-structure." Epstein (*C. A.* 11, 749) and Schwarzschild (*C. A.* 12, 249) have treated only the case where the relativity correction is negligible. Instead of using, like E. and S., the method of sepn. of the variables in the Hamilton-Jacobi equation, which fails completely for relativity motion in an elec. field, K. makes use of the general astronomical method of perturbations. It is shown that it is possible to obtain from the angle variables which describe the unperturbed motion (cf. Schwarzschild) a set which shall describe the perturbed motion to any degree of approximation. In these variables, Schwarzschild's quantum conditions can be applied. This method is only outlined, and will be given in more detail later. With a weak elec. field the components of the fine-structure of a line are split into one or more sharp, polarized components, that are originally displaced according to the square of the voltage. Then new components appear, with intensity increasing as the square or a higher power of the voltage. With increasing field strength the components come closer and closer to the position assigned by the non-relativity treatment, where the displacement is proportional to the first power of the voltage, as observed by Stark. The method of applying Bohr's correspondence principle to get the intensity and polarization of the components is indicated.

F. C. HOYT

The broadening of the mercury line 2537 by gases of different densities. CUR. FÜCHTBAUER AND G. JOOS. *Physik Z.* 21, 694-9(1920).—The broadening of spectral lines due to gas d. was first explained by H. A. Lorentz as follows: The wave trains of practically undamped vibrations are interrupted from time to time by collisions of the emitting or absorbing mols. with the surrounding gas mols. Füchtbauer and Hofmann (*C. A.* 8, 1050) showed by measurements on lines of alkali metals broadened in N that the number of interruptions computed from the broadening is much greater than the number of collisions of metal atoms with N mols., and suspected that the elec. field of the N mol. had some influence on broadening. It is of interest to investigate the broadening of a line which shows no Stark effect and the Hg absorption line 2537 is accordingly examd. for broadening in 10 to 25 atms. of CO_2 , N_2 and H_2 . The broadening due to Doppler effect in these expts. is about 0.003 Å and is negligible compared to the width of 0.3 to 1.0 Å caused by pressure. Measurements are made on the absorption coeffs. at the max. of absorption (m_λ) which are assumed inversely proportional to the half-value width of the line (ν). A Cd spark in air is photographed with a quartz spectrograph after the light passes an 82-mm. tube of Hg vapor under pressure. For example, an exposure was made with 25 atm. gas pressure and suitable vapor pressure followed by 3 exposures at 10 atm. and different vapor pressures. The latter were chosen so that the absorption with 25 atm. would lie in the range and the conditions for equal absorption were found by interpolation.

Writing $(\mu\kappa)_1/(\mu\kappa)_2 = (P_2/P_1)^\kappa$ where P represents the gas pressure, these expts. show that the exponent κ approximates unity, i. e., with const. vapor pressure, $\mu\kappa$ is inversely proportional to the d. of the gas producing line broadening, or, in other words, the line broadening is directly proportional to the gas pressure. This broadening may perhaps be explained by the disturbing effect of the elec. field of rapidly moving mols., i. e., the broadening points to the existence of a change in spectral lines which is caused by a heretofore unknown action of very rapid variations in field strength. W. F. M.

Temperature dependence of infra-red characteristic frequencies of ammonium salts. O. REINKOBBER. Danzig-Langfuhr. *Z. Physik* 3, 318-28(1920); cf. *C. A.* 15, 338.—R. measures the effect of temp. changes on the selective reflection of several NH_4 salts for a range of -175 to 120° in the infra-red. With decreasing temp. there is an increase in intensity and the selective bands become sharper and are shifted toward shorter wave lengths. F. C. HOYR

The infra-red rotation spectrum of the halogen hydrides. A. KRATZER. *Z. Physik* 3, 289-307(1920).—The energy of a rotating and at the same time vibrating mol. is quantized so as to depend on the quantum number of the rotation and of the vibrations of the nuclei. The quantized rotational energy has the usual form, $(h^2/8\pi^2 I) m^2$, but the law of force for the oscillations is taken to be in the form of a power series in the reciprocal of the distance. This gives a form of the series agreeing with the measurements of Imes (*C. A.* 14, 3366) on HF, HCl and HBr. The line in the middle that is missing corresponds to a change of the rotational quantum number from 1 to 0, indicating that a state with no rotation is very improbable. F. C. H.

Infra-red spectra of isotopes. F. W. LOOMIS. *Astrophys. J.* 52, 248-56(1920).—Although two of the many attempts to find differences between the wave lengths of spectrum isotopes of Pb have been successful, the differences found are very small and no theory has been published which accounts satisfactorily for even their order of magnitude. Much larger effects should be expected for any vibration in which 2 atoms or nuclei are the principal masses concerned instead of one atom and an electron. The infra-red absorption bands of HCl and HBr would be expected to be doublets due to isotopes since Aston (*C. A.* 14, 3578) has shown that Cl is a mixt. of isotopes of at. wts. 35 and 37 with possibly a very little 39 and that Br is a mixt. of at. wts. 79 and 81. Furthermore the structure of these absorption bands has been explained so exactly by Kemble (*C. A.* 14, 3365) as to leave little doubt that the central frequency of the "fundamental" band (at 3.46μ for HCl and 3.91μ for HBr) is the frequency of vibration of the charged halogen atom and the H nucleus along their line of centers. L. shows that the frequencies of the doublets due to isotopes should be approx. proportional to the sq. root of $(m_1 + m_2)/m_1m_2$; in which m_1 is the mass of the H nucleus and m_2 that of the charged halogen atom; hence the band lines due to HCl^{35} and HCl^{37} should differ by $1/1330$, and those due to HBr^{79} and HBr^{81} should differ by $1/6478$. Examin. of the absorption spectra of HCl and HBr and HF plotted by Imes (*C. A.* 33, 3366) shows that each rotational quantum line in the first harmonic of the HCl spectrum has on the long-wave side a satellite of less intensity and sepd. from it by an av. measured interval of 14\AA . or 4.5 wave numbers, which agrees within the probable error of measurement with the calcd. value of 4.3 wave numbers. These satellites are the predicted lines due to the heavier isotope. F has been shown to be pure, at. wt. 19.00, and the absorption spectrum of HF accordingly consists of single lines. In the case of HBr the computed sepn. are smaller than for the harmonic of HCl and the lines of sep. isotopes have not been resolved. W. F. MARGORIS

Action of red and infra-red rays on phosphorescent substances. MAURICE CURIE. *Compt. rend.* 172, 272-4(1921).—Certain substances like alk. earth sulfides and ZnS under the action of illumination rich in short wave lengths are excited to phosphor-

essence, which is suddenly extinguished under the action of long waves. With ZnS a slight recovery has been observed. Whereas previous observers have used exciting and extinguishing radiations in succession, in these expts. they are applied simultaneously, ultra-violet light of wave length 0.386μ being obtained from a Hg lamp through a filter of Ni oxide and infra-red from an arc lamp through a Cu oxide filter. The extinction radiation is concd. in a small area on the substances studied, either phosphorescent materials in a soln. of celluloid in acetone spread on glass or silk colored with org. fluorescent substances. Under these conditions: (1) With ZnS a black spot is observed on a luminous background and if the plate is moved the restitution of light is observed in the train of the dark spot. This recovery varies in intensity and duration with the phosphorescent material. (2) With fluorescent substances such as uranium nitrate, double sulfate of U and K, Ba cyanoplatinate, esculine, fluoresceine, etc., one observes neither spot nor variation in brightness, where the infra-red rays are concd. Expts. are in progress to test a recent theory which seeks to explain these phenomena as a resonance agitation of the S atoms. W. F. MCGGERS

The blackening of a photographic plate as a function of intensity of light and time of exposure. P. S. HELMICK. *Phys. Rev.* 17, 135-46(1920).—The object has been the expression of the blackening of a photographic plate as a function of the intensity of monochromatic light and time of exposure to light, other factors being const. Such an expression finds practical application in photometry of monochromatic sources. By exposing a plate to a light source of unknown intensity for any known length of time, measurement of the resulting blackening will enable the unknown intensity of light to be calcd. Three emulsions, a slow one (Seed 23), a rapid one (Seed 27x) and a very rapid one (Seed Graflex) were coated on plate glass and illuminated for various lengths of time with various intensities of monochromatic light of wave length 450, 550 and 650μ . The results are given in curves where density $D (= \log_{10} \text{opacity})$ is plotted against \log_{10} intensity, and are found to be well represented, for a given emulsion and wave length, by the empirical equation for blackening, $D = (1/a) \log [b - (b-1)e^{-CT}]$, in which $\log c = A + B \log I + c \log I^2$ and a, b, A, B , and C are const. A graphical method employing a monographic chart is described for detg. these const. Schwarzschild's exponent p (in the expression $I t^p = \text{const.}$ for equal blackening) is shown to be equal to $(B + C \log I)^{-1}$ and is found to vary from 0.7 to 1.95 according to the emulsion, wave length and intensity. The procedure of "calibrating" plates and detg. intensity by this method is described in detail. W. F. MCGGERS

The light scattered by argon. LORD RAYLEIGH. *Compt. rend.* 171, 1002.—A note calling the attention of J. Cabannes (*C. A.* 15, 343) to recent work of the author on the degree of polarization of the light scattered by A (*C. A.* 14, 3591). R. H. L.

Determination of the structure of crystals (WYCKOFF) 2. Distortion in thermionic tube circuits (POCOCK) 4. Recent advances in science (X-ray reflection from crystal powders) (PEIRCE) 2. Crystal structure of magnesium oxide (WYCKOFF) 2. Application of the theory of space groups to the study of the structure of crystals (WYCKOFF) 2. The state of aggregation of the elements and the atomic model (HENGLER) 2.

BIJL, H. J. VAN DER: The Thermionic Vacuum Tube. New York: McGraw-Hill. 391 pp. 232 illus. For review see *Elec. World* 77, 725(1921).

4—ELECTROCHEMISTRY

COLIN G. FINK

High-frequency induction steel furnace. E. F. NORTHROP. *Chem. Met. Eng.* 24, 309-11(1921).—A crucible furnace heated by an induced current of high frequency and capable of handling from 50 to 60 lbs. of steel has proved successful. The furnace

consists of a conical crucible 10.5 in. high, 10.5 in. top diam. and 4.5 in. bottom diam. set into a water-cooled inductor coil of the same shape and sepd. from it by a thin layer of elec. insulation, micanite, and a thin layer of heat insulation. The coil and crucible are surrounded with heat insulation and set into an asbestos box. Steel is melted rapidly because of its high elec. resistance and high hysteresis loss. Because of low elec. resistance, brass, Au, Ag and Cu are best melted in a C or graphite crucible, in which case the current is induced in the crucible and the contents are in turn heated by transmitted heat. Unique features of the furnace are that the exterior of the furnace is at all times at room temp. and that the molten metal is agitated by induced electro-magnetic forces maintaining uniformity of temp. and compn. A special 20-kw. converter set consisting of 12 condensers, a transformer with external reactance and a discharge gap converts current of ordinary frequencies to frequencies of 10,000-25,000 cycles per second.

O. A. HOUGEN

Operating details of electric furnaces. EDWARD T. MOORE. *Chem. Met. Eng.* **24**, 171-6(1921).—Desirable operating details of elec. furnaces are specified in a report of the Elec. Furnace Comm. of the Assoc. of Iron and Steel Elec. Engineers based on a questionnaire submitted to steel mfrs. operating elec. furnaces. Transformers exceeding 22,000 volts are undesirable because a special type of oil switch is required for safely rupturing the current. Automatic control of electrodes is essential to reduce surges of power to a minimum; surges increase electrode consumption and shorten the life of contacts. Max. density of current in cables is 900 to 1000 amp. per sq. in.; in bus bars, 700 to 850 amperes per sq. in. Dual voltage control is desirable in large furnaces where the increased cost is warranted, a high voltage for the heating period and a low voltage for refining period. Low reactance is undesirable because of the high short-circuiting current. With an air core a reactance as high as 43.6% is desirable, increasing the short-circuiting current 229% and reducing the power factor to 90%. A special ring which cools gases to below kindling temp. has been designed for reducing electrode consumption. Tables are given showing the allowable variations in graphite and carbon electrodes as to length, diam., threads and resistance. Av. elec. resistance of C electrodes should not exceed 0.002 ohm per cu. in. at 20°; of graphite electrodes, 0.00036 ohm.

O. A. HOUGEN

Electric melting in non-ferrous industry. ANON. *Iron Age* **107**, 770-3(1921).—A detailed review. There are 408 elec. furnaces installed in the non-ferrous industries (U. S.) vs. 261 a year ago.

C. G. F.

Electric vs. gas melting of brass. H. M. ST. JOHN AND A. E. RHOADS. *Brass World* **17**, 81-3(1921).—Polemical. Includes valuable cost data.

C. G. F.

Electrometallurgical procedure for the working up of zinc dust and scrap metal to pure metal. HEINRICH PAWECK. Vienna. *Z. Elektrochem.* **27**, 16-21(1921).—The Zn dust is dissolved in dil. H_2SO_4 and an anolyte containing 4% Zn and 5% free H_2SO_4 prepd. The neutral catholyte contains 10% Zn. These solns. are electrolyzed in a diaphragm cell between a Pb anode and an Fe cathode, until the Zn concn. of the catholyte sinks to 4%. The catholyte now contains 4% Zn and 5% free H_2SO_4 and the anolyte 4% Zn and 10% H_2SO_4 . The former is transferred to the anode section of the cell, and the latter brought up to a 10% Zn concn. with Zn dust neutralized, and employed as the catholyte and electrolysis continued. In an expt. cited, the area of the cathode on one side was 1.4 dm² and that of the anode on one side was 1.65 dm²; the electrodes were sepd. by 6 cm., and a current of 4.1 amp. was employed. The energy consumption per kg. Zn is estd. at 3.38 kw. hr. Scrap Zn is worked up to pure Zn by making it the anode in a diaphragm cell. Of the impurities present, only Fe goes into soln. The Cu, Sn and Pb, as well as the Fe as basic salt, pass into the anode slimes. The energy consumption per kg. Zn amounts

to 3.23 kw. hr. for the 1st 8-10 hrs. and thereafter, when the process has become stabilized, 2.5 kw. hr.

H. JERMAIN CREIGHTON

Nitric acid manufacture by Schönher's arc process. FUSAJIRO KODERA, ICHITARO KITAWAKI AND BUICHI YOKOVAMA. *J. Chem. Ind. (Japan)* 23, 1010-5(1920).—The inner tube of the furnace was 6 in. in diam., the arc could be prolonged to about 13 feet and total length of the furnace was about 20 ft. with a capacity of 100 kw. With this furnace, when the arc was most stable the following results were obtained: With 5,000 v., 72 c. ft. of air supplied per min., arc voltage 2,703, 30 amps., power required 74 kw. and arc length 13 ft., 1.8% (by vol.) of NO gas was produced, a yield of 82 g. per kw. hr. The gas from the furnace is then passed through a multitubular boiler, H₂O cooler, an oxidation chamber, and finally, absorption towers. This method, although tedious, gave over 42% HNO₃. It is, however, more economical to stop absorption when the acid concn. reaches about 35%. On account of the leakage of acid-eggs, etc., the quantity of HNO₃ obtained from the absorption towers was far less than that calcd., and the real yield of HNO₃ per kw. hr. was about 65 g. 3% of the total energy supplied to the furnace was consumed in the formation of NO, 60% in cooling H₂O and 12% by the boiler.

S. T.

Black nickel solutions. II. J. HAAS, JR. *Metal Ind.* 19, 73-4(1921); cf. *C. A.* 15, 789.—Tabulated exptl. results show the effect of increasing the concn. of one salt at a time in the plating baths. Na₂SO₄ increases the conductance and decreases the ionization of Ni(SO₄). A S-free bath giving good results contains: Water 1 gal. (3.78 l.); NiCl₂ 6 oz. (170 g.); NaCl 2 oz. (56.7 g.); Rochelle salts 1 oz. (28.3 g.); ZnCl₂ 3/4 oz. (21.2 g.).

W. H. BOYNTON

Electrical method of charging storage batteries. ANON. *Elec. Rev.* 78, 503(1921).—The feature of this equipment is the use of three units for each machine, the third unit being used as a hooster to allow the storage batteries to be discharged directly back into the line. In this way the capacity of the equipment is increased without altering the generator set. A diagram is given of the "set up."

D. I. GLEIM

Aluminium electrolytic (lightning) arrester. A. G. RAMSEY. *J. Inst. Elec. Eng. (London)* 57, 306-11(1920).—In its simplest form the Al electrolytic arrester consists of 2 Al plates immersed in a suitable electrolyte. The most important characteristic of the cell is the critical voltage. This is dependent on the production of a film of aluminium hydroxide on the surface of the plates by subjecting them to chemical and electrochemical action. Below the critical voltage, the film allows only an exceedingly small current to flow but at a higher voltage the current is limited ultimately only by the resistance of the electrolyte. The most satisfactory electrolyte is composed of 10% (NH₄)₂B₄O₇, 10% concd. glycerol and 80% H₂O. "The chemistry of the subject is not well understood, but the glycerol appears to react in some manner, as the soln. becomes acid and must be neutralized again as before. It seems probable that this effect is due to oxidation of the glycerol to form an organic acid." D. MACRAE

Cottrell electric precipitation plant at the Imperial mint. TAKESHI SHIBATA. *J. Chem. Ind. (Japan)* 23, 1058-65(1920).—Fume nuisance caused by H₂SO₄ used in sepg. Au and Ag in the Imperial mint, Osaka, could never be eliminated in spite of the uses of settling chambers and wash towers. Finally Cottrell's elec. pptn. plant was installed. Detailed description of both general arrangement and power plant are shown in two diagrams and exptl. results are given in full.

S. T.

Cottrell system of dust and fume precipitation. ANON. *Engineering* 111, 94-7 (1921).—A detailed description of a very successful Cottrell system to clear effluent gases from a contact sulfuric acid plant at Holten Heath, England. The treater consists of earthed Pb plates and cross-shaped high-tension bars hanging in a lead chamber. The system is flexible but ordinarily runs at 55,000 v., obtained by mechanical

rectification of a 50-cycle a. c. A short description of the contact process is also given.

M. KNOX.

Distortion in thermionic-tube circuits. L. C. POCKOCK. *Electrician* 86, 248(1921).—Two forms of distortion are possible. First is that in which the various components of a complex wave form are differently amplified or attenuated to an extent depending upon their frequencies, such as is continually encountered in telephone circuits because of the varying value of any complex impedance with frequency. The second type is that in which an impressed pure sine wave is reproduced as a sine wave of the same frequency with added harmonics. This case is likely to occur in a transmitting circuit where sinusoidal variation of the transmitter resistance does not cause a pure sine-wave current to be formed. Distortion in the grid circuit and in the plate circuit are treated mathematically.

W. E. RUDER

Transformer-vault location, construction and equipment. H. J. CLARK. 455-6 (1921).

C. G. F.

Calcium (BRACH) 2. Commercial manganese alloys (HÄBERT) 9. An electric furnace for the separation of arsenic in Lockemann's method for determining arsenic (BIRCKENBACH) 1.

ADDICKS, LAWRENCE: Copper Refining. New York: McGraw-Hill Book Co. 206 pp. \$3.

Chromous chloride. M. C. TAYLOR. U. S. 1,369,204, Feb. 22. CrCl_3 is made by passing an elec. current through a soln. of CrCl_3 containing 1-2% free HCl in a cell having sep. anode and cathode compartments, to effect reduction.

Electric fixation of nitrogen. G. T. SOUTHGATE. U. S. 1,369,714, Feb. 22. A portion of the gases introduced into an elec. arc for fixation are supplied through small channels extending through vertical electrodes of willow charcoal. Within these electrodes are core pipes surrounded by bushings of asbestos, through which another portion of the gas supplied to the arc is conducted to a central portion of the arc zone and ejected horizontally so as to bend the arc outward. A reduced pressure is preferably maintained in the reaction space and the manner in which the gas is supplied from sep. streams obviates undue heating or need of cooling jackets. N and O or mixts. of N and O in various proportions may be supplied separately through the different tubes or air may be supplied through each.

Thin iron plate. S. YUNOKI and M. KUSUMI. Japan 36,255, April 27, 1920. Pure thin Fe plate (1-10 mm.) is prepd. by electrolyzing a soln. of 750 g. crystd. FeCl_3 and 700 cc. H_2O acidified weakly with HCl and adding Al at 80-100°. Fe is used as the positive pole and Cu plate as the negative one and a current of 1.5 v. and 10 amp. per 1 sq. dm.

Electrolytic metal-cleaning solution. T. A. EDISON. U. S. 1,369,271, Feb. 22. An electrolyte adapted for use in an electrolytic cell for cleaning metals preliminary to electroplating is formed of Na_2SO_4 or K_2SO_4 soln., nearly satd. and rendered alk. with caustic alkali.

Gold plating. M. SAITÔ. Japan 36,099, April 7, 1920. To prep. an electrolyte for gold plating, 22.5 g. Au, 11.25 g. Ni, 16.65 g. Pt and 7.5 g. Ir are dissolved separately in aqua regia and neutralized with NH_4OH . The 4 solns. are mixed and a small quantity of KCN and Na_2PO_4 is added.

Electrolytic apparatus for alkali chloride. J. IMANARI. Japan 36,057, March 31, 1920. An app. based on the Hg method.

Electric arc hearth furnace. M. R. TREMBOUR. U. S. 1,369,578, Feb. 22.

5—PHOTOGRAPHY

LOUIS DERR

Colloid chemistry and photography. I. Development as nucleus detector. H. LÜPPO-CRAMER. *Kolloid-Z.* 28, 25-9(1921).—The ripening of AgBr emulsions brings an incipient reduction of the AgBr, and the light causes a pulverization of the salt. Physical developers act more strongly on the fine "nuclei" than chemical developers do, and it is claimed that the phenomena of development of the latent image afford a sufficiently valid proof of the presence of these nuclei.

L. DERR

Colloid chemistry in photography. R. E. SLADE. *Third Rept. on Colloid Chemistry, Brit. Assoc.* 1920.—Discusses photographic emulsions, colloidal Ag and Ag deposits, gelatin and gum.

JEROME ALEXANDER

Colloid in photography. H. W. GREENWOOD. *Third Rept. on Colloid Chemistry, Brit. Assoc.* 1920.—A brief review.

JEROME ALEXANDER

The reclaiming and utilization of old films. MAURICE DESCHERNS. *Rev. prod. chim.* 23, 591-2(1920).—A review of various methods for the recovery of used films (extr. of the cellulose ester, biochem. methods, chem. methods), and of the utilization of the recovered products for fresh films or for varnishes and "dopes."

A. P.-C.

The blackening of a photographic plate as a function of intensity of light and time of exposure (HELMICK) 3.

Photographic films. F. SCHORFF and O. DORENDAHL. *Brit.* 154,902, Nov. 19, 1920.—As a substitute for celluloid or transparent paper, what is known in Germany as "Glashautpapier" (glass-skin paper) or "Zellophane" (cellophane) or "Zellstoffglashaut" (cellulose glass-skin) is used. The material is obtained from viscose and forms a flexible and tough skin similar to celluloid and gelatin and is not inflammable.

Photographic developers. J. HAUFF & Co. *Brit.* 154,198, Nov. 22, 1920. The patent relates to photographic developers of the aminophenol or aminocresol class made with the addition of sulfite and soda or potash wherein alkali salts of the carboxylic or sulfonic acids of the *o*- or *p*-aminophenols or the *o,p*-diaminophenols are present. In order to restore to such solns. containing carboxylic and sulfonic acids their original developing powers a further quantity of free caustic alkali is added. A developer instanced contains muriated *p*-aminosalicylic acid (100 g.), sulfite free from H₂O (500 g.), normal lye of 5-fold strength (210 cc.) and H₂O (5790 cc.). For use this stock soln. is dild. with an equal or double quantity of H₂O and a further quantity of ordinary soda lye added according to the exposure and requirements.

6—INORGANIC CHEMISTRY

H. I. SCHLESINGER

Nomenclature of binary inorganic compounds. JOHN SEBELIEN. *Tidskrift Kem.* 17, 242-5(1920).—Comments on the subject matter assigned to a committee on nomenclature appointed at a meeting of Scandinavian natural science investigators held in Christiania in 1916.

A. R. R.

Trithiocarbonates and perthiocarbonates. E. W. YROMAN. *J. Chem. Soc.* 119, 38-54(1921).—Pure hydrosulfides of the alkali metals were prepd. by action of H₂S on EtOH solns. of the ethoxides and by addition of S to these, the pure alkali polysulfides were obtained. All operations were carried on in a current of dry H₂. By reaction with CS₂ the Na, K and NH₄ salts of H₂CS₃ and H₂CS₄ were obtained in

cryst. form and analyzed. The trithio salts are yellow to red, very deliquescent, but stable in dry air free from CO_2 . Their aq. solns. are distinctly red, while the perthio-carbonates, which also are yellow, yield yellow solns. It was found that $\text{Na}_2\text{S} + \text{CS}_2 + \text{EtOH} = \text{Na}_2\text{CS}_3 + \text{EtOH} + 5700 \text{ cal.}$ and $\text{Na}_2\text{S} + \text{CS}_2 + \text{EtOH} = \text{Na}_2\text{CS}_4 + \text{EtOH} + 8550 \text{ cal.}$ Since $\text{Na}_2\text{S} + \text{S} + \text{aq.} = \text{Na}_2\text{S}_{\text{aq.}} + 1400 \text{ cal.}$, assuming the same heat evolution in alc. soln., $\text{Na}_2\text{CS}_3 + \text{S} + \text{EtOH} = \text{Na}_2\text{CS}_4 + \text{EtOH} + 4280 \text{ cal.}$ From aq. solns. red-yellow needles of $3\text{Ca}(\text{OH})_2 \cdot \text{CaCS}_3 \cdot 9\text{H}_2\text{O}$ and from alc. soln. similar needles of $\text{Ca}(\text{OH})_2 \cdot \text{CaCS}_3 \cdot 2\text{H}_2\text{O}$ were obtained. CaS_2 was converted to $\text{CaCS}_3 \cdot 2\text{Ca}(\text{OH})_2 \cdot 8\text{H}_2\text{O}$, dark red needles, by a current of H satd. with CS_2 and evapg. the soln. *in vacuo*. Addition of Et_2O to alc. solns. pptd. oils, which crystd. slowly; the crystals formed yellow aq. solns., which gave the reactions of perthio salts but contained much thiosulfate. BaCS_3 , yellow microcrystals, is more stable than the other salts. Its soln. dissolved 1 atom of S per mol. but solid BaCS_4 could not be isolated. $\text{SrCS}_3 \cdot 4\text{H}_2\text{O}$, dark red needles, becoming yellow on drying *in vacuo*, is much more sol. in water than the Ba or basic Ca salts. $\text{SrCS}_3 \cdot 8\text{H}_2\text{O}$, yellow crystals, forming a yellow aq. soln., which dissolves no more S; sol. in EtOH and pptd. by Et_2O as a red oil. The pure Mg salts could not be prepd. H_3CS_3 probably forms the insol. red oil noted by several observers; H_3CS_3 probably exists and is sol. in water.

A. R. MIDDLETON

The alkali metal cyanides. JULIUS MEYER. *Z. anorg. allgem. Chem.* 115, 203-17 (1920).—The cyanides of Li, Cs and Rb have been isolated in pure dry form, analyzed and studied for the first time. LiCN was prepd. by adding HCN to LiOH or metallic Li suspended in abs. Et_2O or benzene and drying *in vacuo*. RbCN and CsCN were prepd. by dissolving the hydroxides in the least possible amt. of H_2O , adding 20 vol. alc., and then HCN. In addition to the following compds. were prepd. for the first time: the argenticyanides $\text{LiAg}(\text{CN})_2$, $\text{RbAg}(\text{CN})_2$ and $\text{CsAg}(\text{CN})_2$; the ferro- and ferricyanides $\text{Li}_4\text{Fe}(\text{CN})_6 \cdot 6\text{H}_2\text{O}$, $\text{Li}_4\text{Fe}(\text{CN})_6 \cdot 4\text{H}_2\text{O}$, $\text{Rb}_4\text{Fe}(\text{CN})_6 \cdot 3\text{H}_2\text{O}$, $\text{Rb}_4\text{Fe}(\text{CN})_6$ anhyd., $\text{Cs}_4\text{Fe}(\text{CN})_6 \cdot 3\text{H}_2\text{O}$ and $\text{Cs}_4\text{Fe}(\text{CN})_6$ anhydrous; and $\text{Rb}_4\text{Mn}(\text{CN})_6$. It is to be noted that these salts of Rb and Cs are isomorphous with the corresponding K salts. The method for the prepn. of the ferrocyanides was to add $\text{H}_4\text{Fe}(\text{CN})_6$ to the carbonate, and of the ferricyanides by shaking silver ferricyanide with the chloride of the metal. By means of measuring the speed of sapon. of EtOAc with the hydroxides and cyanides of all 5 of the alkali metals, the degree of hydrolysis of the cyanides in aq. soln. at concns. between 1 and 0.1 N were obtained. All the hydroxides and all the cyanides gave identical results, and the results checked with the values for degree of hydrolysis calcd. from the dissoc. const. of H_2O and HCN, as follows for dilns. 1, 2, 5 and 10, resp.: at 18° —0.37, 0.52, 0.83, 1.17; at 25° —0.40, 0.50, 0.89, 1.25.

G. L. CLARK

Disodium hydrogen phosphate dodecahydrate. D. L. HAMMICK, H. K. GOADBY AND HENRY BOOTH. *J. Chem. Soc.* 117, 1589-92 (1920).—Certain peculiarities of the dodecahydrate having led to the suspicion that the analysis of the system by Shiomi (*C. A.* 3, 2779) was incomplete, the authors examd. the various hydrates by means of the heating and cooling curves. The dibydrate was prepd. by boiling finely powdered dodecahydrate with EtOH, the heptahydrate by fusing the appropriate mixt. of 12- and 2-hydrate and cooling. The hydrates were suspended in xylene in jacketed tubes immersed in a glycerol bath. The following invariant points were found: 2-hydrate-anhydrous salt, 94.97° ; 7-hydrate-2-hydrate, 48.09° ; 12-hydrate-7-hydrate, 35.0° . (Shiomi, 36.45° ; 48.0° ; 95.2° .) A sharp break in the curve was observed at 29.6° and it was found that the dodecahydrate exists in 2 forms; the β -form passes into the α -form at 29.6° and the latter into 7-hydrate at 35° . The eutectic, β -dodecahydrate-ice, was found at -0.47° , agreeing closely with the value, 0.45° , found

by Rüdorff (*Ann. Phys. Chem.* [ii], 122, 337(1864)). The soly. curves of the two 12-hydrates were detd. and the transition temps. found to agree closely with those from the heating and cooling curves.

A. R. MIDLINGTON

Reaction between copper and nitrogen peroxide. H. V. TARTAR AND W. L. SIMON. *J. Am. Chem. Soc.* 43, 494-500(1921).—The authors restudied this reaction which Sabatier and Senderens (*Bull. soc. chim.* [3] 9, 668(1893); *Ann. chim. phys.* [7] 7, 399(1896)) stated to form Cu nitroxyl, Cu_2NO_2 . The prepn. of pure materials and the app. used are described in detail. Hydrated cuprous oxide was prepd. and its compn. found to correspond closely to $4\text{Cu}_2\text{O} \cdot \text{H}_2\text{O}$, confirming Mitscherlich. This was reduced by CO; pure Cu was prepd. by reduction of CuO both by CO and by H_2 . Cu reduced by H_2 reacted with N_2O_5 much more rapidly than that reduced by CO but both appeared to give the same end product. The data show that Cu_2NO_2 is not formed and that the product is a mixt. As the atom ratio O:N absorbed was closely 3:1, and on adding water 90% of the N was found as nitrate and 10% as nitrite, surface formation of anhydrous cuprous nitrate is believed most probable.

A. R. M.

Tetrahasic polymolybdates. S. POSTERNAK. *Compt. rend.* 172, 114-7(1921); cf. C. A. 14, 2306; 15, 993.—The current classification of molybdates into ortho, meta and para has no basis in fact. There are two groups only: the hexabasic polymolybdates, of which the ortho and para are particular cases, and the tetrabasic polymolybdates, which result from the former through hydrolytic rupture of their chains. An ammonium trihydroxy tetramolybdate $\text{NH}_4\text{O}(\text{OH})_2\text{Mpo}(\text{O} \cdot \text{MoO}_3)_4 \cdot \text{OH} \cdot 5\text{H}_2\text{O}$, is obtained by mixing 100 cc. of 10% NH_4 molybdate with 16 cc. of molybdic liquor, or with 25 cc. of 2N H_2SO_4 and 10 g. $(\text{NH}_4)_2\text{SO}_4$. This salt loses $5\text{H}_2\text{O}$ *in vacuo* over H_2SO_4 and 1 mol. more when heated at $130-60^\circ$. On recrystg. twice from 4 parts water at 75° , and removing insol. NH_4 trihydroxy hexamolybdate it is transformed into the triammonium trihydroxy tridecamolybdate previously described. A soln. in which $\text{MoO}_3:\text{NH}_3 = 13$ is obtained after 6 days by dialysis of molybdic liquor. It, therefore, contains NH_4 pentahydroxy tridecamolybdate, $\text{NH}_4\text{O}(\text{OH})_5\text{MoO}(\text{O} \cdot \text{MoO}_3)_9 \cdot \text{H}_2\text{O} \cdot \text{MoO}(\text{OH})_3$, which has not been obtained in cryst. form, but from which NH_4NO_3 ppts. the triammonium trihydroxy salt.

A. R. MIDLINGTON

The hyposulfites. ANRÉ DUBOSC. *Rev. prod. chim.* 23, 303-10, 370-4, 433-6, 501-2, 557-62, 593-6, 629-32, 661-5, 725-7(1920); 24, 11-3(1921).—A general review comprizing a historical sketch of the discovery of hyposulfites, various theories brought forward as to their constitution, properties of hyposulfurous acid and its salts, methods used for their prepn. on a com. scale, application of hyposulfites of Ca in the sugar industry, brief mention of various less important hyposulfites (NH_4 , Mg, K), industrial uses of hyposulfites, and their methods of analysis.

A. P.-C.

The precipitation of some of the rare earths by creams of insoluble oxides and carbonates, based on the principle of hydrolysis. ARTHUR C. NICH AND J. W. BURNS. Queen's Univ. *Can. Chem. Met.* 5, 69-74(1921).—The object of the investigation was to predict the precipitant for each of the rare earths, after measuring the H-ion concn. of some salts of the rare earths, and the OH-ion concn. of various oxides and carbonates. E. m. f. measurements made on 0.01 N solns. of the nitrates showed that the order in regard to H-ion concn. was Th, Ce (ic), Nd, Pr, Ce (ous) and La. From this and from a series of measurements on the OH-ion concn. of various oxides and carbonates it is predicted that: (1) Certain oxides, such as FeO , CoO , etc., having a very small concn. of OH ions would not ppt. Th completely. (2) Other oxides, etc., such as CdO , HgO , etc., would ppt. nearly all of the Th. (3) Some oxides, such as ZnO , PbO , Pb_2O_3 and the carbonate PbCO_3 would ppt. Th and Ce (ic) completely and leave the other rare earths in soln. (4) Certain oxides, giving an appreciable concn.

of OH ions, such as Ag_2O , MgO , MgCO_3 would be needed to sep. Nd and Pr from La. (5) As lanthanum hydroxide is a stronger base than NH_4OH , a strong base would be needed to ppt. it completely. Experimental work along these lines resulted in the development of the following scheme of analysis: Treat the soln. with H_2S or SO_2 to reduce Ce to the cerous condition. Boil out the excess, treat the soln. in an atm. of CO_2 with PbCO_3 , ZnCO_3 , CuCO_3 , Pb_2O_3 , or ZnO in slight excess and filter. (1) The precipitate contains thorium as the hydroxide. Dissolve and reppt. as the hydroxide, wash, ignite and weigh. (2) The filtrate from (1) contains Ce, La, Nd and Pr. Treat with a small amt. of KMnO_4 , slight pink, heat to boiling and add a slight excess of PbCO_3 , MnCO_3 , ZnCO_3 , or Pb_2O_3 with stirring and filter quickly. (3) The ppt. from (2) contains the Ce as ceric hydroxide. Det. in the same way as Th. (4) The filtrate from (3) contains Nd, Pr and La. Treat with a slight excess of MgO , Ag_2O , or MgCO_3 . Heat only to 60° ; filter. (5) The ppt. from (4) contains Nd and Pr. Dissolve and subject to fractional pptn. with ammonia. (6) Treat the filtrate from (5) with NaOH and det. La in the same way as Th.

P. E. B.

The role of crystal water and the structure of the alums. Rejoinder to Schaefer and Schubert. L. VEGARD. *Ann. Physik* 63, 753-8(1920); cf. C. A. 14, 373.—Another chapter of a heated discussion, chiefly concerning claims to priority.

A. R. M.

Some thiocyanates of silver. R. CERNATESCU. *Bull. sec. sci. acad. Roumaine* 6, 53-6(1920).—By dissolving AgSCN in the alkali thiocyanate the following complex compds. were obtained: NaSCN.AgSCN ; 3NaSCN.AgSCN ; $\text{NH}_4\text{SCN.AgSCN}$; $5\text{NH}_4\text{SCN.AgSCN}$. All were well crystd. and decompd. by much water. BaCl_2 pptd. no Ag.

A. R. M.

Silicic acid. VICTOR LERNER. *J. Am. Chem. Soc.* 43, 391-6(1921).—Sand, over 99% SiO_2 , was ground in a ball mill 400 hrs. when 85% had a diameter less than 0.004 mm. When this material was shaken with cond. water and allowed to settle in tall cylinders, 28-32 mg. per l. were permanently in soln. after 2-3 weeks; the Tyndall effect and rapid Brownian movement were shown by the soln. after several weeks. Selected orthoclase similarly treated showed similar colloidal properties both in water and in EtOH , although less than 0.5% K_2O went into true soln. At 400° in high-pressure bombs water slowly gelatinized fused-silica ware and at 500° transparent quartz crystals. From expts. upon the effect of very high pressure on pptd. SiO_2 it is concluded that the silicic acids are purely hypothetical and can only be formulated as $x\text{SiO}_2 \cdot y\text{H}_2\text{O}$, in which the quantities vary from a true soln. of SiO_2 in water, successively through the highly hydrated gels which pressure alone will convert from a water content of nearly 98% to a silica with only a few % of water.

A. R. MIDDLETON

HOWE, JAS. LEWIS: *Inorganic Chemistry for Schools and Colleges*. 2nd Ed. revized. 3rd Ed. of "Inorganic Chemistry According to the Periodic Law," by F. P. Venable and J. L. Howe. Easton, Pa.: The Chemical Publishing Co. 443 pp. \$4.

ROSCOE, H. E. AND SCHORLEMMER, C.: *Treatise on Chemistry*. Vol. II. *The Metals*. 5th Ed. revized. New York: The Macmillan Co. \$12. Cf. C. A. 14, 3606.

7—ANALYTICAL CHEMISTRY

WILLIAM T. HALL

Electrometric titrations. W. D. TREADWELL AND L. WHISS. *Helvetica Chim. Acta* 2, 680-97(1919).—In electrometric titrations the end-point is obtained most readily if, as comparison electrode, a cell is chosen such that the e. m. f. between it and the

titration electrode is 0 when the end-point is reached and the current is reversed upon the addition of more reagent. Thus in the titration of Ag^+ with NaCl soln. it is advantageous to use instead of a normal or standard electrode a AgCl electrode which may be attached to the shaft of an app. for electrolysis with rotating electrode so that the electrode also acts as stirrer. Similarly titrations are described (1) of H_2S using as comparison electrode a ppt. of Ag_2S in contact with a Ag wire and a soln. of dil. NaNO_3 and titrating with AgNO_3 , (2) of mercurous ions using a suspension of Hg_2Cl_2 in the comparison electrode and titrating with NaCl , (3) of mercurous ions using bromide instead of chloride in the same way, and (4) of cuprous ions using Cu_2I_2 and NaHSO_4 soln. in the comparison electrode and titrating with KCNS . Using insol. electrodes, the titrations of Zn with ferrocyanide, Fe with dichromate, and of U and V with permanganate are described.

W. T. H.

The theory of electrometric titrations. W. D. TRRADWELL. *Helvetica Chim. Acta* 2, 672–80(1921).—Independently of the work of Kelley and Conant, von Bichowsky, Oesterheld and Honneger, and others, quite a number of electrometric titrations have been studied at the Zürich Technische Hochschule. In this paper the mathematical relations involved are explained with particular reference to the titration of Ag^+ with NaCl soln. When a considerable quantity of foreign salt is present, the end-point is obtained a little too soon and this appears to be due to the formation of Ag complexes.

W. T. H.

End-point in oxidation titrations determined by means of the potentiometer. I. M. KOLYNOFF. *Chem. Weekblad* 16, 408–16(1919).—The theory of oxidimetric titrations and the sharpness of the end-point in relation to the magnitude of the equl. const. are discussed.

J. C. S.

The volumetric estimation of mixtures of acids and bases, and of polybasic acids or bases. HENRY THOMAS TIZARD AND ALFRED REGINALD BOHRER. *J. Chem. Soc.* 119, 132–42(1921).—Simple relations applicable in all but exceptional circumstances, are pointed out and illustrated. The concn. of H^+ in a soln. of 1 equiv. of a weak acid, HA_1 , and x equiv. of a weak acid, HA_2 , to which 1 equiv. of a strong base, BOH , has been added is found from (1) $(C_H)^2 = K_1K_2[x - (1 - y)]/y$, where y is the equiv. of A_1 . For a dibasic acid or a mixt. of 2 acids in equiv. proportions x is 1 and (2) $C = \sqrt{K_1K_2}$. To calc. the effect of the addition of small amts. of alkali near the half-way point the titration of a dibasic acid or mixt. of 2 acids in equiv. proportions, the relations (3) $C_H^2/K_1K_2 = [(1 - y)(y - z)]/[y(1 + z - y)]$, and (4) $K_1/K_2 = y(y - z)/[(1 - y)(1 + z - y)]$, are formulated for the addition of $(1 + z)$ equiv. of BOH to one each of HA_1 and HA_2 . By assigning arbitrary values to K_1/K_2 , then calc. y from (4) for different values of z , and finally substituting in (3) values are obtained of C_H/K_1K_2 . A table is given for various values of K_1/K_2 and various additions of alkali. When K_1/K_2 is 10^4 a 1% error in the amt. of alkali alters C_H ten-fold, and a wide choice of indicators is possible. For $K_1/K_2 = 10^2$ it requires 10% excess alkali to halve C_H and the accuracy of the titration is uncertain with the correct indicator. To halve C_H with 1% excess of alkali, K_1/K_2 must be at least 2.5×10^4 , similarly for 0.1% excess $K_1/K_2 = 2.5 \times 10^6$. For bases at the half-way point C_{OH} , K_1/K_2 and $C_H = K_W/K_{OH} = K_W/K_1K_2$, where K_1 and K_2 are the dissociation consts. of the bases. For a mixt. in which x is not 1 C_H (C_{OH} for bases) = xK_1K_2 and to titrate to 1% as above $K_1/xK_2 = 2.5 \times 10^4$, to titrate to 0.1% $K_1/xK_2 = 2.5 \times 10^6$. These conditions apply in all cases where the neutral salt effect can be neglected. In the titration of a single acid or base the second dissociation const. is K_W . The theory was applied to the titration of 0.1 N NH_4OH soln. in the presence of an approx. equiv. amount of aniline, the titration of β -picoline in aq. soln. and with ammonia, and mixt. of phenol and AcOH . C_H (or C_{OH}) was detd. and the proper

indicator then chosen. Where K_1/K_2 was less than 2.5×10^4 no accurate results were obtained, chloroacetic acid could not be titrated with AcOH, trichloroacetic could be estd., as K_1/K_2 was only slightly less than 2.5×10^4 . The theory also holds for the neutralization of phosphoric acid. Succinic acid cannot and maleic acid can be titrated to a half-way point, and the latter can also be titrated in the presence of a weak acid, although succinic acid cannot. If a salt chosen as a regulator is that of a di- or trihasic acid whose dissociation consts. are widely different, a small excess of acid or base will have a large effect, with Na_2HPO_4 an excess of 1 part in 1000 of NaOH or H_3PO_4 changes nearly two-fold; where K_1/K_2 is small a similar excess has negligible effect.

ARTHUR F. KAUFÉ

Electroanalytical separation of copper, antimony and tin. F. FOERSTER. Dresden. *Z. Elektrochem.* 27, 10-6(1921).—The electrolytic deposition of Cu, the sepn. of Cu from Sh and the sepn. of Cu and Sn, in solns. contg. HNO_3 and $\text{H}_2\text{C}_2\text{H}_4\text{O}_6$ as well as the deposition of Sn from alk. oxalate solns, have been studied. From the results obtained the following procedure for the separation of Cu, Sh and Sn has been developed: The electrolyte, containing in 40 cc. the 3 metals, 5 cc. HNO_3 (d. 1.4) and 5 cc. 50% $\text{H}_2\text{C}_2\text{H}_4\text{O}_6$, is electrolyzed for 1 hr. with a current of 1.5 amp. in a Frary-app. (cf. *C. A.* 2, 838, 737). The deposited Cu is dissolved from the cathode with HNO_3 and $\text{H}_2\text{C}_2\text{H}_4\text{O}_6$ and deposited a second time to recover any Sh that might have separated along with it. Each soln. from the Cu deposition is neutralized with KOH and 50 cc. 10% $\text{H}_2\text{C}_2\text{O}_4$ added, heated, and the Sh pptd. with H_2S . The two Sb ppts. are united, dissolved in 80 cc. Na_2S , 30 cc. 30% KCN soln. added, and the Sb is deposited with a current of 0.6 amp. at 70° . The filtrate from the larger quantity of Sb_2S_3 (containing all the Sn) is evaporated to a small vol., neutralized with 50% KOH, made alk. with 2 cc. additional, oxidized with 1 cc. 3% H_2O_2 , boiled, diluted to 150 cc., and then electrolyzed for 3.5 hrs. at $80-85^\circ$ in a Frary-app. with a current of 5 amp. The Sn is deposited on a wire-gauze cathode. The following results were obtained with the foregoing procedure: present, 0.4196 g. Cu, 0.0462 g. Sh, 0.4040 g. Sn; found, 0.4202 g. Cu, 0.0460 g. Sh, 0.4045 g. Sn.

H. JERMAIN CREIGHTON

Analytical control of electrolytic zinc production. H. F. BRADLEY. *Chem. Met. Eng.* 24, 461(1921); cf. *C. A.* 14, 3197.—Further details are given for the analysis of leach soln. and for the detn. of Cu, Cd and Zn in Zn dust.

W. T. H.

A new process for the estimation of small quantities of chromium in steels. B. S. EVANS. *Analyst* 46, 38-42(1921).—Dissolve 4 g. of metal in 50 cc. of 6 N H_2SO_4 . To the hot soln. add HNO_3 to oxidize Fe^{++} and boil till red fumes are removed. Add 25 g. $(\text{NH}_4)_2\text{HPO}_4$, 250 cc. of water and more nitric acid if a ppt. forms. Heat to boiling and add dropwise satd. KMnO_4 till a permanent ppt. or red color is obtained, then add twelve drops more and boil 15 min. Meanwhile place 120 cc. of 20% NaOH soln. in a large beaker, add to it 14 drops of satd. KMnO_4 and boil this soln. a few minutes, adding more KMnO_4 if necessary to give a purple color. When the soln. of the steel has boiled 15 min. remove the NaOH soln. from the hot plate, add 10 cc. of 5% MnSO_4 soln. to destroy the MnO_2 and pour the acid soln. of the steel into the alkali with stirring. Transfer the soln. to a 500-cc. flask and make sure that it is alkaline. Add 10 cc. of AcOH and test to make sure that soln. is now acid. Make up to the mark, mix, and filter through a dry filter. Place 100 cc. in a Nessler tube and in another tube place 80 cc. of water, 20 cc. of 9 N H_2SO_4 and add 0.01 N $\text{K}_2\text{Cr}_2\text{O}_7$ until the colors match. If Ni or Co be present, pour 100 cc. of the soln. into a flask, heat to boiling and add NaOH to ppt. $\text{Ni}(\text{OH})_2$ and $\text{Co}(\text{OH})_2$, cool, filter, catch the filtrate in a Nessler tube, and finish as above. With very small quantities of Cr, about 0.25 cc. of 0.01 $\text{K}_2\text{Cr}_2\text{O}_7$ in excess will be used, as can be detd. by a blank expt.

ARTHUR F. KAUFÉ

Some modifications of the de Nolly electric apparatus for the determination of carbon in ferrous alloys. BÉGIN. *Ann. chim. anal. chim. appl.* 3, 15-6(1921).—The detn. of C by the de Nolly method (cf. *C. A.* 5, 1888, 2807; 6, 1114, 3243) requires considerable manipulative skill. The suggestion is made that the current used should be controlled by throwing some incandescent lamps into the circuit, because 12 amp. may be required in some cases and 8 amp. is sufficient in others. The conical flask in which the combustion of the alloy takes place should be provided with a 2-way stopcock, the contents of the flask should be well chilled after the combustion, and the final titration of the excess NaOH should take place in the original flask. During the titration, the H_2SO_4 should be added slowly and the contents of the flask should be well shaken toward the end. Bi_2O_3 is a better oxidizer in this method than is PbO_2 . The results obtained are too low if the sample contains 3.5% C or more. W. T. H.

The volumetric determination of iron in the presence of considerable hydrochloric acid. MEURICE. *Ann. chim. anal. chim. appl.* 13, 23-5(1921).—The usual method for titrating Fe^{++} with KMnO_4 in the presence of HCl is to titrate in the presence of excess Mn^{++} . The analysis may be effected without the aid of excess Mn^{++} if the titration takes place in the presence of Br^- and is continued until the vapors obtained by passing a current of air through the soln. will give an intense blue with iodo-starch soln. The theory of the method is that the Br^- ion is not oxidized by MnO_4^- until the Fe^{++} has been entirely oxidized and there is no appreciable effect of MnO_4^- on HCl without the formation of Br_2 . W. T. H.

Tentative methods for chemical analysis of alloys of lead, tin, antimony and copper. ANON. *Proc. Am. Soc. Testing Materials* 20, I, 589-98(1920).—*I. General method. Detn. of Pb.* Dissolve 1 g. of the finely divided alloy by boiling in a covered beaker with 70-100 cc. of an acid soln. made by dissolving 20 g. of KCl in 500 cc. of H_2O and adding 400 cc. of HCl (d. 1.20) and 100 cc. of HNO_3 (d. 1.42). Evap. to 50 cc. Add 5 cc. of HCl, cool in ice-water until the bulk of PbCl_2 has crystd. out, then add slowly with stirring 50 cc. of 95% alc. and cool in ice-water for 10 min. Add 50 cc. more alc. keeping the soln. cool for 20 min. longer and filter. Wash 3 times by decantation with a soln. made by mixing 400 cc. of 95% alc. and 100 cc. of HCl and wash the paper twice with this mixt. Transfer the PbCl_2 back to the beaker and wash the paper first with hot H_2O and finally with hot acid ammonium acetate soln. made by mixing 500 cc. of NH_4OH (d. 0.90) and 500 cc. of H_2O and acidifying with 80% AcOH . Heat until the PbCl_2 is dissolved. Add 15 cc. of satd. soln. of $\text{K}_2\text{Cr}_2\text{O}_7$ and heat until the ppt. has become orange. Filter on a weighed Gooch crucible, wash with H_2O , alc. and Et_2O and dry at 110° . Calc. % Pb by the empirical factor 0.6375. *Detn. of Cu.* Evap. the filtrate from the PbCl_2 ppt. to dryness. Add 10 cc. of KOH soln. (100 g. of KOH in 500 cc. of H_2O) and after a few min. add 20 cc. of 3% H_2O_2 . If necessary add more KOH until the soln. is alk. Heat on the water bath for 20 min., add 10 g. of ammonium oxalate, 10 g. of oxalic acid, and 200 cc. of H_2O . Pass in H_2S for 45 min. with soln. near to boiling. Filter at once and wash the ppt. with hot H_2O , uniting the washings with the filtrate. Wash the sulfides of Cu and Sb back into the beaker with the least possible amt. of H_2O , add 10 cc. of KOH soln., heat on the water bath until the dissolved matter is black, filter through the same paper, and wash with hot H_2O . Ignite the paper and ppt. in a small casserole, dissolve in HNO_3 (d. 1.42), boil to expel nitrous fumes, neutralize with Na_2CO_3 , add a few drops of NH_4OH and titrate with standard KCN soln. (3.5 g. of KCN in 1800 cc. of H_2O and standardized against Cu). Instead of titrating, the Cu may be detd. electrolytically after adding 5 cc. of concd. H_2SO_4 . *Detn. of Sb.* Add 50 cc. of concd. HCl to the above KOH soln. of Sb_2S_3 and boil to a small vol. to expel AsCl_3 . Add 25 cc. concd. HCl and 1 g. of KClO_4 and boil until colorless. If necessary filter

through glass wool. Cool, add 1 g. of KI, 1 cc. of CS_2 , and titrate with 0.1 *N*- $\text{Na}_2\text{S}_2\text{O}_3$ soln. *Detn. of Sn.* Concentrate the filtrate and washings from the pptd. sulfides of Cu and Sb to 200 cc. and add 5 g. more of oxalic acid if the amt. of Sn is above 0.5 g. Electrolyze until the soln. reacts alk. using a current of about 0.5 amp. Wash the deposit with H_2O and alc., dry at 110° , and weigh. *Detn. of As.* Weigh 1 g. of sample into a 250-cc. distn. flask and add 10 cc. of FeCl_3 soln. (d. 1.43), 60 cc. of concd. HCl , 20 cc. of H_2O and 5 g. of KCl . Connect the flask with a condenser, heat slowly until soln. is complete and boil down to as small a vol. as possible, catching the distillate in a 400-cc. beaker. Cool the flask, add 50 cc. of concd. HCl and redistill as before, catching the distillate in the same beaker. Cool the distillate and pass in H_2S for 1 hr. Allow the As_2S_3 to settle and filter on a Gooch crucible. Wash twice with HCl (1:4), 4 times with cold H_2O , 3 times with alc., and 4 times with CS_2 . Dry at 110° for 10 min. and weigh. Dissolve As_2S_3 with $(\text{NH}_4)_2\text{CO}_3$ soln., wash thoroughly with H_2O , dry at 110° , and reweigh. The difference in weights multiplied by 0.60911 gives the % of As. *II. Rapid method for control work. Detn. of Pb.* Dissolve 1 g. of alloy in 20 cc. of concd. H_2SO_4 , heat the soln. until the metal is completely decomposed, and finally boil for $\frac{1}{2}$ hour. Allow to cool slightly but not below 60° and add 100 cc. of H_2O in which has been dissolved 5 g. of tartaric acid. Allow to stand 2 hrs. and filter on a Gooch crucible. Wash with a soln. made up as follows: Mix 300 cc. of concd. H_2SO_4 with 1800 cc. of distd. H_2O and add to this hot soln. 1 g. of $\text{Pb}(\text{OAc})_2$ dissolved in 300 cc. of distd. H_2O ; let stand 24 hrs. and siphon through asbestos. Retain the filtrate and these washings for the detn. of Cu. Remove the filtrate and wash the PbSO_4 with dil. alc. Set the Gooch crucible inside a porcelain crucible and ignite for 5 min. with the full heat of a Tirrill burner. Weigh as PbSO_4 . *Detn. of Cu.* To the filtrate from the PbSO_4 add NH_4OH (sp. gr. 0.90) until the soln. is slightly alk., then add 2 cc. of concd. H_2SO_4 . Heat to boiling, add 2 g. of Na_2SO_4 and when dissolved, add 1 g. of KCNS dissolved in 10 cc. of H_2O . Shake the soln. and allow the CuCNS to settle 1 hr. keeping the soln. hot. Filter, wash with cold H_2O and ignite paper and ppt. in a porcelain crucible. Dissolve in concd. HNO_3 , add 5 cc. concd. H_2SO_4 , and evap. until fumes of H_2SO_4 are evolved. Dil. to 100 cc., add 1.5 cc. of concd. HNO_3 and det. Cu by electrolysis. The Cu may also be detd. by dissolving the above ignited ppt. in HNO_3 , boiling to expel nitrous fumes, neutralizing with Na_2CO_3 and titrating with KCN as in the general method above. *Detn. of As.* In a 300-cc. flask dissolve 0.5 g. of the finely divided alloy in exactly 8 cc. of concd. H_2SO_4 . Heat to boiling, cool, add about 5 cc. of H_2O and a bulk of about 0.5 cc. of granulated pumice. Boil the covered soln. gently for 5 min. or until the odor of SO_2 has disappeared. Finally, being careful to have 5 cc. of H_2O present, cool the soln. and cautiously add 20 cc. of concd. HCl . Insert in the flask a rubber stopper fitted with a thermometer and delivery tube which is connected with an S condenser one curve of which is nearly filled with H_2O and the end of which dips into about 75 cc. of H_2O . Heat the soln. to gentle boiling for 10-15 min., keeping the vapor temp. at 107° for at least 5 min. Wash out the condenser and add an excess of about 2 g. of NaHCO_3 . Dil. to 200 cc., warm to about 27° , and titrate with standard I soln. *Detn. of Sb.* Cool the soln. which remains in the flask after the As distn., add 130 cc. of cold recently boiled distd. H_2O to which has been added 3 cc. of concd. HCl , and titrate with standard KMnO_4 . *Detn. of Sn.* If the sample does not contain 14% of Sb, add enough dissolved SbCl_3 to make 14% Sb. Then add exactly 6 cc. of concd. H_2SO_4 and 60 cc. of concd. HCl and add about 6 in. of No. 14 pure Fe wire cut into 2-in. lengths and cleaned with dil. HCl . Boil gently 30 min., add about 6 in. more wire and boil 30 min. longer. Remove from the heat, close the flask loosely and allow about 2 min. for all air to be expelled by H and acid vapors. Stopper the flask

and place in cold H_2O , cooling to about 20° . Transfer the soln. to a beaker, dil. to 300 cc. and titrate quickly with standard I soln. S. G. SIMPSON

The dissolving of iron oxide minerals. E. LITZGUR. *Ann. chim. anal. chim. appl.* 3, 16-9(1921).—As is well known, many Fe ores and ignited Fe_2O_3 are very slowly dissolved by aq. HCl. Raising the temp. and increasing the concn. of HCl increases the rate of dissolving. Expts. with several difficultly sol. products show that by satg. the soln. with HCl gas in the cold and then heating in a sealed vessel it is very easy to effect complete soln. Care must be taken in opening the vessel after this treatment and if the mineral contains MnO_2 or any other constituent from which gas is likely to be evolved, it is advisable to heat gently, cool, open the vessel and then heat more strongly in the closed vessel. Details are given for constructing suitable app. for this heating with HCl under pressure. W. T. H.

Tentative method for ultimate chemical analysis of chrome ores and chrome brick. ANON. *Proc. Am. Soc. Testing Materials* 20, I, 647-51(1920).—I. General method. Dry the fine powder at 110° for not less than 1 hr. Cool in a desiccator. Fuse 0.5 g. of the sample with approx. 10 g. of fused $KHSO_4$ in a Pt crucible. The most refractory ores should be thoroughly fused in $1\frac{1}{2}$ -2 hrs. Allow the crucible to cool in the air and dissolve the fusion in 200 cc. hot HCl (1:1), boiling until the soln. acquires a clear green color. Evap. to dryness on a water bath and bake at exactly 120° until free from HCl fumes. Moisten with hot HCl (1:1), evap., and bake as before. Dissolve in 200 cc. hot dil. HCl and filter SiO_2 . Ignite and weigh the SiO_2 , detg. the SiO_2 by treatment with HF and H_2SO_4 . Any appreciable residue should be fused with $KHSO_4$ and added to the filtrate. Dil. the filtrate to 500 cc. and ppt. Fe, Al, Cr and Ti with NH_4OH in very slight excess. Filter, dissolve in HCl, and reppt. Again filter the combined hydroxides and dissolve in HNO_3 . Evap. in a casserole adding crystals of $KClO_4$ from time to time until the Cr is completely oxidized. Dil. with hot H_2O and again ppt. with NH_4OH , filtering as before. Repeat the oxidation 2 or 3 times until the filtrate shows no further traces of Cr. Combine the filtrates and evap. to 500 cc. Add H_2SO_4 until the soln. changes to a brilliant green color and heat to boiling. Add a very slight excess of NH_4OH , filter, wash, ignite, and weigh as Cr_2O_3 . The hydroxides of Fe, Al and Ti are ignited and weighed. Fuse the combined oxides with a small amt. of $KHSO_4$, dissolve the fusion in dil. H_2SO_4 , reduce with H_2S and titrate with $KMnO_4$. Det. the Ti colorimetrically and calc. the Al by difference. To the combined filtrates from the hydroxide pptn. add Br, allow to stand a few min. and then add sufficient NH_4OH to ppt. the Mn. Boil, filter, ignite, and weigh as Mn_2O_3 . From the filtrate ppt. the Ca with NH_4OH and $(NH_4)_2C_2O_4$ and det. in the usual way either by ignition to the oxide or by titrating with $KMnO_4$. Det. the Mg in the filtrate from the Ca ppt. in the usual way as $Mg_2P_2O_7$, and use the J. Lawrence Smith method for the detn. of alkalies. II. Rapid routine method. Fuse 0.5 g. of the fine dry sample with 8-10 g. of Na_2O_2 in a Ni or porcelain crucible. Leach out with cold H_2O , boil 15 min., cool, and add 100 cc. H_2SO_4 (1:1). Cool, and titrate the Cr with ferrous soln. and $KMnO_4$. To detn. Si and Fe, fuse 0.5 g. of the sample in a Ni crucible, leach out with cold H_2O , acidify with HCl and evap. to dryness. Take up with 200 cc. of H_2O and add 10 cc. HCl. Filter SiO_2 and if necessary repeat the evapn. and filtration. Make the filtrate alk. with NaOH and add 5 cc. Br. Digest $\frac{1}{2}$ hr. on a steam bath. Filter $Fe(OH)_3$ on asbestos, dissolve and reppt. Filter again, dissolve in hot HCl, reduce with $SnCl_2$ and titrate with $KMnO_4$ in the usual way. S. G. SIMPSON

The sampling and estimation of quicksilver ore. C. N. SCHUETTE. *Mining Sci. Press* 122, 293-5(1921).—In the formation of most deposits of Hg ore two factors appear to have been dominant: (1) a relatively impervious stratum directing or limit-

ing the upward flow of the mineralizing solus., and (2) the porosity of the rock underlying this impervious gap. Examples of Hg mines in Calif., Nev. and Texas are given. S. states that Hg ores cannot be sampled in the manner usual with other types of ores, and recommends panning by experienced persons, which method will check assays within 0.1%.

A. H. HELLER.

Tentative methods for chemical analysis of limestone, lime, and hydrated lime. ANON. *Proc. Am. Soc. Testing Materials* 20, 1, 628-33(1920).—Weigh out 0.5 g. of the substance and in the case of limestone or hydrated lime ignite in a Pt crucible for 15 min. or more with a blast lamp. Transfer to an evaporating dish, mix to a thin paste with H_2O , add 5-10 cc. of concd. HCl and digest until soln. is complete. Evap. to dryness. Treat the residue with 15-20 cc. HCl (1:1), filter and wash the SiO_2 . Repeat the evapn., unite the ppts. of SiO_2 , ignite, and weigh. For great accuracy, volatilize the SiO_2 with HF. Ppt. Al and Fe as hydroxides from the filtrate with NH_4OH in the usual way. Reppt., ignite, and weigh as $Fe_2O_3 + Al_2O_3$. Fuse the combined oxides with 3-4 g. of $NaHSO_4$, dissolve in dil. H_2SO_4 , evap. to fumes, dil. with H_2O , filter any sepd. SiO_2 , ignite, weigh, and add to the value obtained above. Reduce the Fe in the filtrate with H_2S , boil out the excess, and titrate the Fe with $KMnO_4$. Calc. the Al_2O_3 by difference. Det. Ca in the filtrate from the hydroxide pptn. by pptg. with $(NH_4)_2C_2O_4$ and NH_4OH in the usual way. Ignite to CaO, dissolve in HCl, dil. to 100 cc., add NH_4OH in slight excess, and filter out any $Al(OH)_3$, correcting the value obtained above. Reppt. the Ca as above and either ignite and weigh as CaO, or titrate the CaC_2O_4 with $KMnO_4$. In the latter case, wash the ppt. from the paper with hot H_2O , add 50 cc. dil. H_2SO_4 (1:10), dil. to 150 cc., heat to 85° and titrate to a pink color. Then add the filter paper and complete the titration. Total volatile matter is detd. by igniting a 1-g. sample over a blast lamp. To det. mechanical moisture, weigh a 1-g. sample upon a tared watch glass and heat at 120° for 2 hrs. Det. SO_2 in a 2-g. sample by dissolving in dil. HCl and pptg. as $BaSO_4$. Det. CO_2 according to the method given in U. S. *Geologic Survey Bulletin* No. 422, whereby a 0.5-g. sample is treated with dil. HCl and the evolved CO_2 is passed through a reflux condenser and then through $CaCl_2$, anhydrous $CuSO_4$, $CaCl_2$, and is finally absorbed by soda lime.

S. G. SIMPSON

Analysis of ammonium sulfate. H. M. LOWE. *Gas World* 74, No. 1911 (Coking and By-Products Sec.), 11-2(1921).—L. reviews the different analytical operations and brings out the sources of error.

J. L. WILBY

A sensitive form of the iodoform reaction. N. SCHOORL. *Pharm. Weekblad* 58, 209-10(1921).—In Kunz's modification (C. A. 15, 488) of the CHI_3 reaction, $(NH_4)_2S_2O_8$ can be used as well as $K_2S_2O_8$. There is intermediate formation of a black iodide of N, which disappears on heating; and the CHI_3 ppt. has a reddish to orange color, which turns to the usual lemon-yellow only after standing several days in the alk. liquid. The reddish ppt. has no perceptible cryst. form. The formation of CHI_3 can be detected in concns. as low as 1:200,000 by the turbidity which appears. In testing Me_2CO , Na_2CO_3 may be used instead of NaOH; but not in testing EtOH. The Kunz modification is not a quant. reaction in the case of EtOH; but with further study it may be expected to throw some light on the mechanism of the CHI_3 reaction.

JULIAN F. SMITH

Critical study of methods for the determination of small quantities of carbon monoxide in the air and in smoke. DANIEL FLORENTIN AND H. VANDENBERGHE. *Compt. rend.* 172, 391-3(1921).—For the detn. of CO when 2% or more of the gas is present, absorption with ammoniacal Cu_2Cl_2 gives satisfactory results. For smaller quantities, the best methods are (1) oxidation by means of I_2O_5 or (2) measurement of the vol. of gas required to bring out the characteristic absorption bands produced by the action

of CO on the hemoglobin of blood. The various precautions necessary in the former method are discussed and the sources of error are pointed out. The conclusion is drawn that the most reliable method depends upon the use of blood as indicated by Ogier and Kohn-Abrest (*C. A.* 2, 2882).

W. T. H.

The determination of hydrogen-ion concentration by the colorimetric method and an apparatus for rapid and accurate work. ERNEST VAN ALSYNGE. *Soil Sci.* 10, 467-79 (1920).—A colorimeter is described consisting of an eyepiece and wooden blocks holding the standard tubes and the unknowns which slide before it. The blocks holding the tubes may have 1, 2 or 3 series of holes and tubes depending upon whether single tube standards, double tube standards or double tube standards and turbid solns. are used. A graph and table prepared by calculn. are given which permit the prepn. of double tube standards having any desired pH between 2 and 10.

W. J. ROBBINS

Gravimetric methods of analysis. XVI. L. W. WINKLER. *Z. angew. Chem.* 34, Aufsatzteil 46 (1921). XXI. Determination of nitric acid.—The nitron method may be simplified by omitting the cooling to 0° and allowing the ppt. to form during 24 hrs. Instead of filtering through a Gooch crucible a wad of cotton in a cup-shaped filter may be used. To 100 cc. of the neutral soln., contg. 0.05 to 0.01 g. of NO₃⁻ add 1 cc. of glacial AcOH, heat to about 65° and add 10 cc. of clear 10% nitron acetate soln. Allow the soln. to stand in the dark for 24 hrs. at room temp., filter, wash with 50 cc. of satd. nitron nitrate soln. and dry 2 or 3 hrs. at 100°. The method gives good results in the presence of SO₄⁻ and IO₃⁻, but if large quantities of Cl⁻ are present, a correction should be applied which varies with the quantity of ppt. and with the concn. of Cl⁻.

W. T. H.

The detection of gaseous hydrocyanic acid in air. A. SIEVERTS and A. HERMSDORF. *Z. angew. Chem.* 34, Aufsatzteil 3-5 (1921).—A strip of filter paper is freshly moistened with a soln. of Cu-benzidine-acetate and is exposed to the air to be tested for a period of exactly 7 sec. A faint blue coloration of the paper indicates the presence of over 15 mg. HCN per cu. m. A deep blue coloration indicates the presence of over 60 mg. HCN per cu. m., a concn. which is fatal to man. NH₃ and HCHO do not interfere with the test. Oxidizing gases interfere but are not likely to be present under ordinary conditions. The solns. of (AcO)₂Cu and benzidine acetate should be prepared separately, kept away from the light, and mixed only when ready for use. They are prepared as follows: Soln. I. 2.86 g. (AcO)₂Cu per l. Soln. II. 475 cc. cold sat. soln. of benzidine acetate made up to 1000 cc. Mix I and II in equal quantities.

S. G. SIMPSON

Remarks on rapid analyses by conductivity measurements. A. HELDRING. *Chem. Weekblad* 18, 96-7 (1921).—Analyses of mixts. of org. acids or of phenols by cond. detns. can be simplified if the liquid in the thermostat is stirred by blowing in air (prewarmed if desired) instead of with a mechanical agitator. Instead of shaking the electrolysis vessel by hand after each addition of acid, the soln. may be stirred by jets of air previously satd. with the solvent (and prewarmed if desired). There is then no loss of solvent, and the vessel need not be taken from the thermostat at all. To attain higher temps. (thus hastening the equil.) without loss of solvent by evapn., aq. solns. of higher sol. alcs. may be used instead of H₂O-EtOH mixts. J. F. SMITH

Studies on the quantitative determination of aniline and its titrimetric diazotization. TH. SABALITSCHKA and H. SHRAEDER. *Z. angew. Chem.* 34, Aufsatzteil 45 (1921).—Several methods for detg. aniline and its salts in aq. soln. were tested. A method suggested by Lunge, which consists of carrying out the diazotization process on a small scale gave the best results. For the diazotization, use *N* NaNO₂ soln. standardized against pure Na sulfanilate (cf. Lunge, *Chem.-Ztg.* 28, 501 (1904), or against pure aniline.

To the soln. contg. not more than 5 g. aniline in 100 cc. add 3 or 4 molar equiv. of H_2SO_4 and dissolve any ppt. by warming. Cool and add the nitrite soln. drop by drop, shaking after each addition. At first the reaction takes place rapidly but it proceeds slowly toward the last. About 1 hr. is required for the entire titration, which is finished when a drop of the soln. gives an immediate blue color with iodo-starch paper after allowing 15 min. for the diazotization of the last of the aniline. The results cited indicate that the method is accurate to about 3 parts in 1000 for 1-g. samples.

W. T. H.

The precipitation of some of the rare earths by creams of insoluble oxides and carbonates (NEISH, BURNS) 6. An electric furnace for the separation of arsenic in Lockemann's method for determining arsenic (BIRCKENBACH) 1. Indicators for carbon dioxide and oxygen in air and flue gas (MILLIGAN, *et al.*) 1. Determination of hydrogen sulfide in waters containing sulfides of calcium—sensitiveness of the reaction between starch and iodine (CHRÉTIEN, VANDENBERGHE) 14. The iodometric determination of copper and its use in sugar analysis (SHAPPER, HARTMANN) 11B.

AUTENRIETH, WILHELM: *Laboratory Manual for the Detection of Poisons and Powerful Drugs*. 5th Am. Ed., translated by William H. Warren. Philadelphia: B. Blakiston's Son & Co.

8—MINERALOGICAL AND GEOLOGICAL CHEMISTRY

EDGAR T. WHERRY AND WALTER F. HUNT

Some remarkable twinnings from the museum of the Ural Mining Institute. M. K. ELYASHEVICH. *Ann. école mines Oural* 1, 114-9(1919).—Photographic reproductions and crystallographic descriptions of some twinnings of native Au.

H. M. GORDIN

Skutterudite from Cohalt, Ontario. T. L. WALKER. Univ. Toronto. *Am. Mineral.* 6, 54-6(1921).—Bright crystals resembling smaltite were measured crystallographically, and found to show the forms *a*, *o*, *d* and *n*. Analysis showed the mol. ratio of (Co, Ni, Fe) to (As, S) to be nearly 2:5. To ascertain if the material was homogeneous, some of the analyzed powder was treated with hot 50% HNO_3 for 3 min., and H_2O then added. About half the powder was dissolved, and the sol. portion showed the ratio of the above constituents 1:2.22, the insol. 1:2.82. Evidently the crystals represent isomorphous intergrowths of smaltite-cloanthite, $(\text{Co}, \text{Ni})\text{As}_2$ and skutterudite, CoAs_2 . Similar relations have been found to exist in other occurrences of Co arsenides. It is noteworthy that analyses of massive smaltite from the same region approach more nearly the theoretical CoAs_2 than do those of good crystals. The pure individual minerals are practically unknown. E. T. W.

Sphalerite in coal pyrite. LEONARD P. DOVE. Univ. N. Dak. *Am. Mineral.* 6, 61(1921).—Sphalerite occurs in nodules of pyrite-marcasite in shale adjoining coal beds at Bicknell, Indiana. The Zn content may reach 0.18%. E. T. W.

Olivine from Etna. FRANCESCO STELLA STARRABBA. *Rend. mem. accad. sci. Acireale* [iii] 9, 41-65(1917).—Small crystals occurring in tuffs are sepd. according to color and crystal-habit into: (I) olivine of a clear green color and fairly transparent, *d.* 3.42, γ_D 1.707; (II) hyalosiderite olivine of a dark brownish green color and almost transparent, *d.* 3.56, γ_D 1.7303. Analysis I corresponds approx. with $4(\text{Mg}, \text{Ca})_2\text{SiO}_4(\text{Fe}, \text{Mn})_2\text{SiO}_4$ and II with $7(\text{Mg}, \text{Ca})_2\text{SiO}_4.3(\text{Fe}, \text{Mn})_2\text{SiO}_4$. The frequent presence of Fe_2O_3 in volcanic olivine is commented on.

	SiO ₂	TiO ₂	Al ₂ O ₃	Fe ₂ O ₃	Cr ₂ O ₃	FeO
I.	37.97	0.05	1.01	5.24	14.26
II.	37.43	0.57	0.71	5.82	trace	19.34
	(Co,Ni)O.	MnO.	CaO.	MgO.	H ₂ O?	Total
I.	0.32	0.54	40.71	0.34	100.44
II.	0.11	0.64	1.00	34.43	0.14	100.19

J. C. S.

Bementite and neotocite from western Washington, with conclusions as to the identity of bementite and caryopillite. J. T. PARDNER, E. S. LARSEN, JR. AND GEORGE STRICKER. *J. Wash. Acad. Sci.* 11, 25-32(1921).—Bementite occurs at a number of localities in western Washington, associated with quartz, rhodonite, and a manganese calcite ($n = 1.660-1.706$). The bementite rock is cut by veinlets of quartz, calcite, manganocalcite, rhodonite, rhodochrosite, harite, and manganophyllite. At one mine the bementite is associated with native Cu. The bementite has: color light gray to grayish brown, darkening on weathering; luster vitreous; transparent in thin splinters; sp. gr. 3.106; H. about 6. Under the microscope it is seen to consist of felted aggregates of fibers or plates: optically —, elongation +, axial angle near 0, indexes of refraction $\alpha = 1.624$, $\beta = 1.647$, $\gamma = 1.647$. Analysis by S. gave: SiO₂ 39.92, MnO 41.58, FeO 4.15, MgO 4.46, CaO 0.40, Al₂O₃ 1.32, H₂O — 0.49, H₂O + 7.90, sum 100.22%, agreeing with the formula $8\text{MnO} \cdot 0.7\text{SiO}_2 \cdot 5\text{H}_2\text{O}$. The optical, physical and chem. properties of "caryopillite" show conclusively its identity with the earlier described bementite. Neotocite forms small veinlets cutting bementite. The neotocite has: color brown to black; luster resinous; fracture conchoidal, brittle, H. about 4. Under the microscope isotropic, $n = 1.45-1.50$. Analysis by S. gave: SiO₂ 37.15, Al₂O₃ and Fe₂O₃ 2.58, MnO 37.00, MnO₂ 2.03, MgO 2.82, CaO 2.86, H₂O 14.07, CO₂ 2.10, sum 100.61%. Part or all of the Fe may be present as FeO, in which case a correspondingly large part of the Mn would have the form MnO. The formula of neotocite is thus $\text{MnO} \cdot \text{SiO}_2 \cdot n\text{H}_2\text{O}$.

S. G. GORDON

A mineral new to New Zealand—pilotite. J. HENDERSON. *New Zeal. J. Sci. and Tech.* 3, 79-80(1920).—An occurrence of pilotite a mile north of Maholnui, Auckland, is described, with 3 analyses.

S. G. GORDON

A mineral related to xenotime from the Manbhhum District, Bihar and Orissa Province. G. H. TIPPER. *Rec. Geol. Survey India* 51, 31-3(1920).—A mineral intermediate in compn. between xenotime and monazite was found at Ara Burro, Kanyaluka Mauza, 3 miles west of Dhalbhumgarh. The physical properties are: color brown, streak pale brown, luster resinous, translucent; sp. gr. 4.55; H. 4-5; fracture uneven, brittle; perfect cleavage parallel to the length of the crystals; form: prismatic crystals, probably orthorhombic. An analysis showed: Yt earths 47.6, Ce earths 5.8, ThO₂ 6.92, P₂O₅ 30.7%. The associated minerals were apatite, forming the bulk of the specimen, a dark orthorhombic pyroxene, and magnetite in small crystals. S. G. G.

Analysis of pickeringite from Opalbanya. VIKTOR ZSIVNY. *Budapest. Z. Kryst. Min.* 55, 629-31(1920).—A fibrous mineral found near the opal mines, presumably formed by alteration of pyrite and the action of the solns. on the adjoining rocks, gave on analysis: Al₂O₃ 9.52, Fe₂O₃ 4.04, MgO 4.06, CaO 0.70, FeO 0.23, SO₂ 36.62, H₂O 45.52, MnO, Na₂O, (NH₄)₂O and P₂O₅ traces, sum 100.59%. This shows the formula to be $\text{Mg}(\text{Al,Fe})_2(\text{SO}_4)_4 \cdot 22\text{H}_2\text{O}$, corresponding to pickeringite. E. T. W.

The growth of an efflorescence of cerium sulfate on Travancore graphite. MURRAY STUART. *Rec. Geol. Survey India* 51, 156-8(1920).—A specimen of graphite from Velland, in the Nedumangad Taluk of Travancore State, developed an efflorescence of canary-yellow Ce sulfate while in a case in the Geological Museum. The graphite contained visible grains of monazite and occasionally pyrite. The monazite was,

however, unaltered and it is believed that the Ce is present in the graphite in some other form. S. G. GORDON

Mineralogical notes. 12, 13. GEORGE W. CARD. *Rec. Geol. Survey N. S. W.* 9, 105-7, 175-88(1920).—The occurrences of a large number of minerals and rocks in New South Wales are listed alphabetically with notes. Analyses are given of anorthoclase, augite, ekmannite, emery, polybasite, amphibole asbestos, beryl, breunnerite, almandine, spessartite, joseite, orthoclase, and rutile. S. G. GORDON

Chondrules and chondritic structure in meteorites. GEORGE P. MERRILL. *Proc. Nat. Acad. Sci.* 6, 449-72(1920).—The various forms of chondrules are described with a critical discussion of the various theories that have been advanced to account for their origin. "Only the chondrules of glass and cryptocryst. or radiating enstatites (*kugelchen*) present the rounded or oval form with smooth rind-like crust and surfaces, with often one or more saucer-like depressions or excrescences such as are consistent with a theory of origin as fused drops of 'fiery rain' (Sorby). Chondrules of a compd. of holocryst. nature, and those porphyritic through the development of olivine or pyroxene phenocrysts in a more or less glassy base are lacking in smooth exteriors; and though often quite spherical in outline, are as a rule more or less irregular and in many instances show unmistakable evidences of an origin of form through mechanical attrition." S. G. GORDON

The pallasite from Mount Dyrning, Singleton, New South Wales. PETER CHIRVINSKII. (Translated by C. Anderson.) *Rec. Geol. Survey N. S. W.* 9, 189-91(1919-1920).—The olivine of the pallasite was analyzed and the composition of the pallasite calcd. S. G. GORDON

The pallasite of Molong, New South Wales, Australia. PETER CHIRVINSKII. (Translated by C. Anderson.) *Rec. Geol. Survey N. S. W.* 9, 192-6(1919-1920).—A calcn. of the compn. of this pallasite is given. S. G. GORDON

Report on the iron-ore deposits of Yampi Sound, Western Australia. A. MONTGOMERY. Dept. of Mines, Perth. 1920. *Bull. Imp. Inst.* 18, 303-4(1920).—The Fe deposits are in the form of huge beds of dense, solid steel-gray cryst. hematite of micaceous structure, interbedded with quartzite and clay slate. The ore is mostly of high grade and free from deleterious impurities. In all but 1 sample, the P is below 0.05%, the amt. allowable for acid open-hearth treatment. R. L. SMILEY

The Pas mineral belt in 1920. R. C. WALLACE. *Mining Eng. Rec.* 25, 109-13(1920).—Recent exploration has shown this district of northern Manitoba to be considerably mineralized and a probable source of several metals. One large low-grade Cu ore body has been developed and smaller Cu deposits are known. A very large mass of pyrite occurs in quartz porphyry. Co minerals, chiefly smaltite and erythrite, and veins containing Au, Pb, Ag and Sb have been found. E. V. SHANNON

Salt Chuck palladium-copper mine. J. B. MERTIE, JR. *Eng. Mining J.* 110, 17-20(1920).—The mine, originally a low-grade Cu prospect, now produces important amounts of Pd. The ores are chiefly chalcopyrite and bornite with less chalcocite and covellite disseminated in shoots in pyroxenite. They also contain some Au, Ag and Pt. Although the minerals appear to be segregations from the pyroxenite magma, as seen in specimens, polished surfaces show them to have been deposited subsequently to the consolidation of the rock by solns. circulating along fractures. Some downward secondary enrichment has taken place. Details of geology, mineralogy and ore treatment are given. The flotation concs. av. over 3 ozs. Pd per ton. E. V. SHANNON

Tin mines of the Quimsa Cruz range, Bolivia. JOS. T. SINGHWALD, JR. *Eng. Mining J.* 110, 986-90(1920).—The range, a series of high glacier- and snow-covered peaks forming the crest of the eastern range of the Andes, is so rugged and so rigorous in climate that, although highly mineralized, it is one of the least explored of the

Bolivian Sn-bearing areas. The rocks of the crest of the range are granites while the slopes are made up of Silurian and Devonian highly metamorphosed shales with intercalated quartzites and sandstones. These rocks are highly fractured and the fractures are the seat of Sn and W veins. Cassiterite and, in some veins, wolframite, are the only minerals of value. An abundance of tourmaline accompanies much of the ore. The mines are enumerated and described. In the Pireo and Central veins much of the cassiterite resembles the shale or slate of which it is a metasomatic replacement. While the mineral is usually very fine-grained, occasional druses show fine cassiterite crystals up to 1 in. in diameter. Rich ores occur at intersections of the main veins with secondary veins. The Chojnacota veins occur as fracture fillings in brecciated shale. The cassiterite ore contains also quartz, sphalerite, chalcopyrite, arsenopyrite, pyrite and limonite. Siderite is the youngest mineral of the veins. The Sorreno ore body is in quartzite and contains few sulfides but much tourmaline. The Caracoles veins occur in granite. The Pacuni mines contain both Sn and W, the W veins being cut by Sn veins. Several of the mines have been acquired by Guggenheim interests.

E. V. SHANNON

The antimony deposits of the Krupanjer district in West Serbia. RUDOLF STRAK. *Montan. Rundschau* 12, 361-3, 381-3, 393-5, 408-9 (1920).—The deposits occur in bedded Paleozoic limestone into which andesite and trachyte have been intruded. The ore is localized near these intrusions, contact metamorphism being, however, not marked. The ore is essentially stibnite, occurring in rhombic needles embedded for the most part in pure white quartz. Oxidized ores, as valentinite and cervantite, occur and also elementary S. The stibnite contains 4 g. Au per ton and traces of Pb, As and Fe. The ores have originated by metasomatic replacement of the limestone by igneous solns. containing silica and Sh. The ore from the mines is hand-sorted into 2 classes, over 36% and less than 14% Sh. The 1st class of ore is sent to Ph smelters while the 2nd class is roasted, the oxide collected in condensing chambers and reduced in a reverberatory furnace to metallic Sh.

R. S. DEAN

Phosphate in Canada. HUGH S. SPENCE. *Canada Dept. Mines, Mines Branch* 396, 156 (1920).—This monograph comprizes a review of the phosphate industry in Canada, the manu. of P products in Canada, a description of the apatite mines, the geology of apatite-bearing districts, the minerals of the mica-apatite deposits (with analyses), and a bibliography of Canadian phosphate. The mica-apatite deposits form irregular, pockety masses enclosed in pyroxenites believed to represent metamorphosed limestones which have been invaded, disrupted, and engulfed by batholithic masses of granite. The origin of the mica-apatite-calcite bodies is probably to be attributed to the agency of late pegmatitic phases of this granite.

S. G. GORDON

The geology and petrology of the Great Serpentine Belt of New South Wales. IX. The geology, paleontology and petrography of the Currahuhula district, with notes on adjacent regions. W. N. BENSON, W. S. DUN AND W. R. BROWNE. Section C—Petrography. W. R. BROWNE. *Proc. Linnæan Soc. N. S. W.* 45, 405-23 (1920).—The igneous rocks of the Currahuhula district are described. These comprize tuffs, rhyolites, basalts, trachytoid quartz keratophyres (with an analysis), quartz trachyte, quartz latite, andesites (with an analysis of an andesitic pitchstone), lamprophyre, dolerite, albite dolerite, and teschenitic dolerite.

S. G. GORDON

The problems of volcanology. HENRY S. WASHINGTON. *Proc. Nat. Acad. Sci.* 6, 583-92 (1920).—The problems of volcanology and their relations to seismology, meteorology, terrestrial magnetism, and geochemistry are reviewed. Among other suggestions, it is urged that a complete and detailed catalog of all active, dormant, or recently extinct volcanoes be made, with hypsometrical and areal data, petrographic characters and order of succession of the lava, types of activity, chronological list of

eruptions with some indications of the degrees of intensity and a bibliography.

S. G. GORDON

An outline of geophysical-chemical problems. ROBERT B. SOSMAN. *Proc. Nat. Acad. Sci.* 6, 592-601 (1920).—The subject-matter of "geophysical-chemistry" may be roughly divided into the properties and reactions of materials at the earth's surface, and the properties and reactions of materials in the earth's interior. These materials may be further subdivided into the individual chemical substances, (minerals, gases, etc.), aggregates of these (igneous rocks, magmas, metamorphic rocks, sedimentary rocks, and the atmosphere), and the larger units (glaciers, batholiths, etc.). Details are given regarding the problems involved, with an outline of necessary researches.

S. G. GORDON

Sulfur near the confluence of the Greater Zab with the Tigris, Mesopotamia. E. H. PASCOE. *Rec. Geol. Survey India* 51, 153-5 (1920).— H_2S is evolved in great quantities from the bed of a stream 24 miles S. S. E. of Mosul.

S. G. GORDON

Notes on the analysis of mineral sulfide water (FAIRCHILD) 14. Crystal structure of magnesium oxide (WYCKOFF) 2.

9—METALLURGY AND METALLOGRAPHY

WILLIAM BRADY, ROBERT S. WILLIAMS

The theory of flotation. REGINALD S. DEAN. *Mining Sci. Press* 122, 291-2 (1921).—Flotation oils possessing a polar group are adsorbed at the air-water interface. From the chem. formula of the oil, it is possible to det. then its flotation qualities. The oils must spread upon water to a layer one molecule thick, which is a characteristic only of polar substances. Their function is to stabilize the froth. Sulfide minerals have a tendency to adsorb gases and hold them tightly as an outer film, whereas silica has not, and calcite adsorbs only the acid gases. Water will not displace the gas, and the mineral, therefore, acts as a weighted bubble. The value of acid in zinc flotation is due to the evolution of H_2S from the sphalerite to give a gaseous envelope. The accelerating action of $CuSO_4$ in floating sphalerite is due to its increasing the ease of soln. of the sulfide. In the flotation of galena from a limestone gang Cd, and stannous salts are harmful; this is explained by their pptn. on the galena. NaOH added to the pulp when coal-tar is being used forms salts with the phenols and cresols present, which are more sol. and hence more polar than the phenols. It is evident that the chemical properties of the flotation oils are more important than the physical properties. Some quantitative figures for the gases adsorbed on minerals are given.

A. H. HELLER

The standardization of materials employed in mining and milling plant. E. A. WRIGHT. *Bull. Inst. Mining Met.* 1921, 1-19, No. 196; *Mining Sci. Press* 122, 361-6 (1921).—The need for standardized specifications for materials employed in mining and milling is pointed out. This involves the necessity for the collection of reliable data and the coöperation of steel-makers, mine and mill managers. Available data on the chem. compn., methods of manuf., and service records are summarized for drill steels, stamp battery components, rolls, balls for mills, rock-breaker jaws, tube mill liners, and dredges.

LOUIS JORDAN

Renison Bell ores. J. H. LEVINGS. *Australasian Chem. Met.* 3, 44-7 (1920).—About 65% of the tin may be recovered from the gossans by gravity concn. The sulfide ores after roasting give a recovery somewhat lower. A preliminary trial showed that flotation of the sulfides to concentrate the tin in the residues was not satisfactory.

R. S. DEAN

The metallurgy of zinc. LEMARCHANDS. *Rev. Metall.* 17, 803-41(1920); cf. C. A. 14, 1952.—The actual mechanism of the reduction of ZnO by C has not been clearly understood. After considering the early work on the subject, L. describes his own exptl. work. He studied (1) the action of C on ZnO in an atm. of pure N; (2) the action of CO on Zn; (3) the action of CO on ZnO. The app. used is described and sketched. It consists essentially of a gas train with proper provision for purifying and drying the incoming, and for analyzing the outgoing gases. The Zn or the ZnO was contained in an electrically heated quartz tube. *Conclusions:* (1) ZnO is reduced by C and by CO simultaneously. (2) The reduction of ZnO by C begins at temps. which depend on the rate of heating, being lower for rapid heating. (3) The temp. of reduction of ZnO by C is governed by the reaction velocity of the heterogeneous system (ZnO + C), that is by the rate at which the 2 substances can diffuse and thus come into contact with each other. (4) The temp. of reduction of ZnO by C is much lower than has been previously believed, as low as 732°. (5) The reaction $\text{ZnO} + \text{C} = \text{Zn} + \text{CO}$ is reversible. It goes from left to right at 600° but only at much higher temps. is the reverse reaction noted. (6) ZnO is reduced by CO much more easily than has previously been believed, even at temps. as low as 350-400°. (7) Values calcd. on the basis of the energy liberated in the formation of these substances agree well with those found exptly.

E. H. DARBY

The development of antimony production. BRUNO SIMMERSEBACH. *Chem.-Zig.* 45, 121-4(1921).—With the outbreak of the war Sb became increasingly important because of its use in munitions. The occurrence, metallurgy (pptn., roast-reduction, leaching and electrolytic processes), and refining are discussed, the applications of Sb in alloys are mentioned, and full data concerning Sb-producing localities of the world are given.

W. C. REAUGH

The metallurgical plant of the "El Oro Mining and Railway Co., Ltd." JOSE CAMPA. *Bol. minero* 9, 592-608(1920).—A detailed description of the equipment and method of treatment employed in a large plant in Mexico extg. by the cyanide process a low-grade quartz ore containing Au, Ag sulfides, and small amts. of Cu compds. The bullion is partly refined before shipping by cupellation in *kunite* cupels 6 ft. in diam.

L. E. GILSON

Reaction between iron sulfide and carbon dioxide. V. M. GOLDSCHMIDT. *Tidskrift Kem.* 17, 215-8, 221-8(1920).—The reaction $\text{FeS} + 3\text{CO}_2 = \text{FeO} + 3\text{CO} + \text{SO}_2$, if practical, is important for a country dependent entirely on imported coal and was, therefore, given serious consideration. In the first place the Nerst equation, $\log K = -(Q/4.571T) + 1.75 \log T + \Sigma C$, was applied to the reaction and then lab. tests were made. ΣC of this reaction comes to 4.2, and Q to 93,160. The values for K are listed for each 100° from 600° to 2000°. From the author's curves it would seem that at 1500° the CO in the gas mixt. comes to 33% and at 1900° to 75%. The reaction requires too high temps. for practical application. Other possible reactions were calcd., starting out with FeS_2 , the formation of gaseous S_2 , Fe_2O_4 , and COS, but in none of these were the answers to the problem promising. By way of analogy the reaction $\text{ZnS} + 3\text{CO}_2 = \text{ZnO} + 3\text{CO} + \text{SO}_2$ was also calcd., giving no encouragement for the use of CO_2 in metallurgical plants. Lab. tests conformed closely to the calcd. results. There was no trace of reaction between CO_2 and FeS under 630° and appreciable reaction set in first at 1150°. The reaction in the direction opposite to that advocated proceeded much better, SO_2 attacking the FeO at 580°. A. R. ROSE

New blast furnace built at Midland (Pa.). ANON. *Blast Furnace and Steel Plant* 9, 132-8(1921); *Iron Age* 107, 570-5(1921).—A description is given of a new 600-ton blast furnace of the Pittsburgh Crucible Steel Co., at Midland, Pa., and the accompanying additions to the pumping station, blowing-engine house, power house, and boiler house.

LOUIS JORDAN

The basic-open hearth process. I. F. I. TOY. *Blast Furnace and Steel Plant* 9, 30, 45-50(1921); see C. A. 15, 355. II. *Ibid* 9, 167-61.—Various modifications of the basic open-hearth process are described. Pouring temp., alloying additions, and deoxidizer are briefly considered. The growth in capacity has outstripped the growth in efficiency in the basic open-hearth process. Possibilities for future improvement are great.

LOUIS JORDAN

Development of the steel industry during the war in Germany. I. HUBERT HERMANN. *Blast Furnace and Steel Plant* 9, 31-5(1921).—Very efficient ore-handling machinery has been installed in many plants owing to labor conditions. Improvements in the cleaning of blast-furnace gases, in ladle-cars and ladles have been effected. A new type of mixer has been introduced, the "shallow-bed mixer," which offers a large surface to the fuel gases and has a correspondingly shallow bath. It is similar to an ordinary tilting furnace. This mixer has been introduced into iron foundries and its product is entirely equivalent to cupola-iron. II. *Ibid* 9, 146-50.—An improvement in the operation of the open-hearth furnace is described. The usual arrangement is such that the air travels through the hearth above the gases. During the "boiling" period the O necessary for the oxidation of the C in the bath is furnished by an excess of air admitted with the gas. In the ordinary arrangement this air lowers the temp. of the flame. A new arrangement permits a changing of the gas and air currents during the boiling period so that the gas current flows along the crown of the furnace whereas the air current is directed towards the bath. The temp. of the bath is maintained and the time required for the heat is shortened. For fuel in open-hearth furnace mixts. of coke-oven and blast-furnace gas, and cold coke-oven gas alone have been used successfully. In a greatly increased production of steel castings, the ratio of crucible steel to elec. steel castings changed more and more in favor of the latter. In 1917, of a total of 349,484 tons, 37.2% was crucible steel and 62.8% was elec. steel. One-third of the elec. steel was made in induction furnaces.

LOUIS JORDAN

Swain's report on smoke in Salt Lake Valley. ANON. *Chem. Met. Eng.* 24, 463-5 (1921).—Following a judicial decision adverse to the smelter, the Court appointed R. E. Swain a Commissioner to decide on the conditions of operation which would permit the operation of the smelters without injury to their surroundings. This article is an abstract of the report of S. and his staff. They recommend: careful bag-filtration of blast-furnace gases; Cottrell pptn. of roaster dusts, etc.; increased temp. of roaster gases which on discharge carry SO₂, heating them by coal furnaces near the base of the stack during the growing season; stack approx. 455 ft. high; max. daily limit of SO₂ discharge of about 100 tons.

JEROME ALEXANDER

Commercial manganese alloys. J. HÉBERT. *Technique moderne* 12, 508-17 (1920).—General review of the properties, methods of prepn. and analysis, and uses of Mn steels and cast Fe, silico-Mn and ferro-Mn, Mn metal, Mn bronzes, and of the uses of Mn ores other than for metallurgical purposes.

A. P.-C.

Some industrial uses of gas [tempering and case-hardening of metals] (BRODIN) 21. The antimony deposits of the Krupanjer district in West Serbia (STRAK) 8.

Ore flotation. W. A. SCOTT. U. S. 1,369,054, Feb. 22. Acids such as HCl or HNO₃ are employed in facilitating ore flotation sepn., by impregnating the air with the acid and then applying it to the ore pulp. Economy of acid is thus effected, especially in the case of ores containing considerable amts. of CaCO₃ or other substances readily reactive with acids. The acid and bubble-forming air may be beaten into the ore pulp from above its surface or may be introduced into the pulp through a submerged permeable material.

Treating cinnabar ore. A. J. GARVER. U. S. 1,369,738, Feb. 22. Cinnabar ore is allowed to descend through a vertical retort over inclined baffles heated by burners beneath the baffles. From the upper portion of the retort fumes are led through an escape pipe to a rotating horizontal inclined condenser containing H_2O , within which the Hg is condensed.

Ferro-silicon aluminium alloy. W. B. D. PENNIMAN and R. S. WHITE. U. S. 1,369,298, Feb. 22. Ferro-Si and Al alloy is made by reducing compds. of Al, Si and Fe, such as feldspar with Fe and C in an elec. furnace.

10—ORGANIC CHEMISTRY

CHAS. A. ROULLER

Recent advances in science—organic chemistry. P. HAAS. Univ. London. *Science Progress* 15, 377–80(1921).—Review, including summaries of recent work on the carbohydrates and the vitamins.

JOSEPH S. HEPBURN

1-Hydroxy-2-benzoylcamphor. A. L. VAN DER VEEN. *Z. Kryst. Min.* 55, 627 (1920).—This substance crystallizes rhombic-bisphenoidal; complete crystallographic and optical data are given.

E. T. WHERRY

Mixed crystals of p,p' -dichloro-, -dibromo- and -dimethylbiphenyl. K. MIELEINER. *Z. Kryst. Min.* 55, 631–4(1920).—The crystallographic constants and the topic axes of these substances are given, striking relationships being shown.

E. T. W.

Camphor synthesis according to patent literature. E. WITTE. *Chem.-Ztg.* 45, 118–21(1921).—A compilation of the more important patented procedures for the manuf. of synthetic camphor, with some remarks relative to their practicality.

W. O. E.

Preparation of isoprene from light camphor oil. YŪSHICHI NISHIZAWA. *J. Tokyo Chem. Soc.* 41, 1043–54(1920).—Japanese light camphor oil contains pinene, dipentene, limonene, and phellandrene, all of which can be used for prepn. of isoprene. Com. light camphor oil, boiling principally at 150–70°, is used. Cracking was done in an elec. oven, at 500°. The oil was placed in the flask with an air condenser (about 75 cm. long), connected to 2 flasks, each collecting different fractions of the distillate. Five different catalysts were inserted in $1/2$ of the condenser, as follows: (1) lamp black impregnated in asbestos, (2) reduced Ag in asbestos, (3) Cu gauze plated with Ag., (4) reduced Ag in pumice, and (5) pumice powder. The following are the amts. in cc. of distillate obtained from the respective catalysts: at 30–50°, 3, 15, 12, 11, 20; 50–60°, 8, 19, 10, 6, 7; 60–70°, 3, 7, 6, 4, 5; 70–80°, 2, 4, 4, 4, 3; 80–90°, 2, 7, 1, 5, 4; 90–100°, 2, 7, 3, 5, 4; 100–110°, 5, 6, 5, 7, 9; 110–120°, 5, 14, 7, 6, 7; 120–130°, 5, 13, 18, 11, 11; 130–140°, 7, 5, 14, 6, 21; 140–150°, 40, 25, ?, 25. The portion distg. under 70° is isoprene. When purified, it b. 37–8, n_D^{20} 1.41073, d_4^{20} 0.690, C 87.5%, H 11.9%. For this fraction, (2) and (5) are the best catalysts, giving 8% and 10%, resp. The chem. compn. and nature of the fraction b. above 70° have not yet been investigated.

S. T.

Preparation of chloropicrin from picric acid and trinitrotoluenes. KENNEDY JOSEPH PREVITÉ ORTON and PHYLLIS VIOLET MCKIE. *J. Chem. Soc.* 119, 31–3(1921).— CCl_3NO_2 (A) was most easily produced in yields up to 93% of the theory according to equation (1) by the action of Cl_2 on picric acid in Na_2CO_3 . Two reactions occurred: (1) $C_6H_3(NO_2)_3OH + 11Cl_2 + 5H_2O \rightarrow 3CCl_3NO_2 + 13HCl + 3CO_2$; (2) $C_6H_3(NO_2)_3OH + 12Cl_2 + 8H_2O \rightarrow 2CCl_3NO_2 + 18HCl + 4CO_2 + HNO_3$, the first being the principal, the second a less important reaction. Picric acid in 4 parts of Na_2CO_3 (17 equivs.) in 50 parts of hot H_2O , was rapidly cooled so that small crystals of Na picrate sepd., held at below 5° and with stirring washed Cl_2 was passed in slowly

(too rapid a stream of Cl_2 tended to produce chlorate). The Na picrate gradually dissolved and ultimately a colorless oil and a colorless soln. were obtained. A may be sepd. or steam-distd. It is sol. at 10° , 0.058 g. in 100 cc. H_2O . *o*- and *p*- $\text{NO}_2\text{C}_6\text{H}_4\text{OH}$, 2,4-(NO_2) $_2\text{C}_6\text{H}_3\text{OH}$, 2,4-(NO_2) $_2\text{C}_6\text{H}_2\text{Me}$, 2,4,6-(NO_2) $_3\text{C}_6\text{H}_2\text{Me}$ when treated with bleaching powder or Cl_2 and alkali gave only low yields of A. ROGER ADAMS

Decomposition of tartaric acid by heat. FREDERICK DANIEL CHATTAWAY AND FRANCIS EARL RAY. *J. Chem. Soc.* 119, 34-7 (1921).—Tartaric acid when heated carefully in a metal bath under a const. pressure of 10-20 mm. melted when the bath reached 150° , and boiled vigorously. As decompn. proceeded the temp. rose to 185° when a little more gas was evolved and the contents of the flask became viscous. On raising the temp. of the bath further to 180° , the action recommenced, gas was given off and a yellow liquid distd. till finally the whole mass disappeared. In the first stage the distillate was H_2O and the residue a lactide, which absorbed moisture from the air, was insol. in C_6H_6 , CHCl_3 or Et_2O and by treatment with KOH gradually gave tartaric acid, or by treatment with EtOH gave Et tartrate; in the second stage, the gas consisted of 1 vol. of CO to 2 vol. of CO_2 and the distillate was a mixt. of HCO_2H , HOAc and AcCO_2H . From 150 g. of tartaric acid 18.8 g. H_2O , 2.4 g. HCO_2H , 49 g. HOAc, 14.1 g. AcCO_2H , 21.3 g. CO and 43 g. CO_2 were obtained. Structural equations are given to explain the formation of all these reaction products. ROGER ADAMS

Bromine compounds of phenanthrene. I. HERBERT HENSTOCK. *J. Chem. Soc.* 119, 55-61 (1921).—When 32 g. of dry phenanthrene (A) in 50 cc. CCl_4 was treated with 67.4 g. of dry Br_2 in 60 cc. CCl_4 , 11 g. of 9,10-dibromophenanthrene (B) sepd. The filtrate on evapn. to dryness in a current of air gave a residue of 10 g.; this was washed with 3 portions of cold petr. ether, then crystd. from HOAc; it consisted of 2(?)*-bromophenanthrene dibromide* (C), yellow needles m. $100-2^\circ$ (decompn.). C heated at 100° till all the HBr was evolved gave 8 g. of a white solid 2(?)*,10-dibromophenanthrene* (D), plates and needles, from EtOH, m. 161° and 162° , respectively. D heated with CrO_3 in HOAc, then poured in H_2O gave 2(?)*,10-dibromophenanthrone* (E), yellow needles from EtOH, m. 203° ; 2(?)*,10-dibromophenanthrone monoxime*, yellow needles from C_6H_6 , m. 239° . A 1% soln. of D in HOAc was treated with fuming HNO_3 till a cloudiness was permanent; after boiling 5 min. and cooling, 2(?)*,10-dibromo-9-nitrophenanthrene* (F) sepd. out, yellow needles from EtOH, m. 188° . F was heated an hour with Sn and HCl, the product washed with hot H_2O , dissolved in warm EtOH, filtered and poured into H_2O , thus forming 2(?)*,10-dibromo-9-amino-phenanthrene* (G), colorless needles, m. 177° ; acetyl-2(?)*,10-dibromo-9-amino-phenanthrene*, from Ac_2O and G at 180° , formed white crystals from EtOH, m. 202° . D with alc. KOH gave scarlet needles of a substance not m. 350° . In the prepn. of B the petr. ether washings were filtered and gave a substance $\text{C}_{17}\text{H}_{12}\text{Br}_2$, yellow needles from EtOH, m. 216° . 2-Ethoxyphenanthrene (H), when brominated and then HBr eliminated, gave 10-bromo-2-ethoxyphenanthrene, colorless leaflets from HOAc, m. 148° . A 3% soln. of H in HOAc with fuming HNO_3 gave 9,10-dinitro-2-ethoxyphenanthrene, yellow prisms from C_6H_6 , m. 247° . ROGER ADAMS

β -Amino- β -phenylpropiophenone. ALEX. MCKENZIE AND FRED BARROW. Univ. Coll., Dundee and Birkbeck Coll., London. *J. Chem. Soc.* 119, 69-76 (1921).—In connection with work on optical activity β -amino- β -phenylpropiophenone (A) has been prepd. by a modified Gabriel synthesis. An attempt to prep. it more directly by the action of PhMgBr on β -amino- β -phenylpropiophenonitrile (B) was unsuccessful, indicating an oxonium compd. as a primary addition product of the Grignard reagent to C:O (cf. C. A. 14, 1543). When 36 g. $\text{H}_2\text{NCHPhCH}_2\text{CO}_2\text{H}$ (C) (prepd. by the method of Posner, *Ber.* 38, 2316 (1905)) and 35 g. $\text{C}_6\text{H}_5(\text{CO})_2\text{O}$ are heated for 2 hrs. at $155-65^\circ$ and the cooled cryst. mass is recrystd. from a mixt. of 60 cc. AcOH and 60 cc. C_6H_6 , there is

obtained 48 g. β -*phthalimino*- β -*phenylpropionic acid* (D), needles from alc., m. 160.5–70.5°, very sol. in hot EtOH or hot AcOH, moderately sol. in C_6H_6 , and almost insol. in hot H_2O ; heated at 320–50° for 30 min. it completely decomps. (CO_2 evolution beginning at 240°), yielding $C_6H_5(CO)_2NH$, $PhCH:CHCOH$, and some $PhCH:CH_2$ (detected by its pronounced odor). *Acid chloride* (E), needles from C_6H_6 , m. 96–7°. *Anilide*, prisms or plates from AcOH, m. 238°, slightly sol. in EtOH. *Methyl ester*, plates from EtOH, m. 92°. When 20 g. $AlCl_3$ is added to a suspension of E (prepd. from 25 g. D and 20 g. $SOCl_2$) in 100 cc. C_6H_6 and the reaction mixt. worked up in the usual manner after standing overnight at room temp. and then heating for 20 min., there is obtained 26 g. β -*phthalimino*- β -*phenylpropionophenone* (F), needles from hot EtOH, m. 116–7°. From 7.5 g. F suspended in 20 cc. EtOH and heated 10 min. on the H_2O bath with 30 cc. N NaOH, is obtained after diln. with H_2O and acidification, β -*benzoyl*- α -*phenylethylphthalamic acid* (G), needles from EtOH, m. 132°, readily sol. in Me_2CO , EtOH or AcOH, moderately sol. in C_6H_6 , and slightly sol. in light petroleum. From 15 g. G heated 30 min. with 60 cc. HCl and 100 cc. AcOH is obtained, after addition of H_2O and sepn. of the oil, a clear soln., the Et_2O ext. of which when made alk. with NH_4OH yields 2.5 g. A, leaflets from C_6H_6 and light petroleum, m. 82–3°, readily sol. in EtOH, C_6H_6 , Et_2O , or $AcOEt$, and slightly sol. in cold light petroleum; is more stable than desylamine, remaining unaltered in a well corked tube for 6 days, after which decompn. begins. *Picrate*, yellow leaflets from EtOH, darken and sinter 175°, m. 193° (decompn.). *Chloroplatinate*, brown needles from dil. HCl, has no definite m. p. but completely decomps. 250°. B, obtained from the chloride of G and $PhNH_2$, plates from aq. alc., m. 122°, readily sol. in EtOH or $CHCl_3$, moderately sol. in C_6H_6 or Et_2O , and sparingly sol. in light petroleum; the additive compd. with $PhMgBr$ when decompd. with NH_4Cl regenerates B. The chloride of G with dry NH_3 and $C_6H_{11}N$ gives amorphous products. $PhCH(NHCHO)CH_2COCl$, prepd. from the corresponding acid (cf. Fischer, Scheibler and Groh, *C. A.* 4, 2822), $AcCl$ and PCl_5 , when dissolved in C_6H_6 , treated with $AlCl_3$ and warmed 1 hr. on the H_2O bath, underwent an unusual reaction (compare with decompn. of D by heat), giving Ph_2CHCH_2COPh , m. 94–5°. The reaction product of $PhCH:CHCOCl$, C_6H_6 and $AlCl_3$ yielded Ph_2CHCH_2COPh and $Ph_2CHCH_2CO_2H$; under various other conditions Kohler, Heritage and Burnley (cf. *C. A.* 4, 2837) obtained varying quantities of Ph_2CHCH_2COPh , $PhCHClCH_2COPh$, and 3-keto-1-phenyl-2,3-dihydroindene. β -*Benzoylamino*- β -*phenylpropionophenone*, prepd. from $PhCH(NHBz)CH_2COCl$, C_6H_6 , and $AlCl_3$, and also from the hydrochloride of A, $BzCl$, and NaOH, lustrous needles from EtOH, m. 152–4°.

H. GILMAN

Formation of derivatives of tetrahydronaphthalene from γ -phenyl fatty acids. GEORGE ARMAND, ROBERT KON AND ARNOLD STEVENSON. Imp. Coll. Sci. and Tech., London. *J. Chem. Soc.* 119, 87–94 (1921).—In a study of the conditions governing the formation of dicyclic structures of the $C_{10}H_8$ type from C_6H_5 derivs. having 4 C atoms in the side-chain K. and S. have shown that derivs. of $PhCH_2CH_2CH_2CO_2H$ and a deriv. of γ -tetrahydrophenylbutyric acid readily lose H_2O , forming hydrogenated naphthalene derivs. *ac*-1-Keto-3-methyltetrahydronaphthyl-3-acetic acid (A), obtained in 12–14-g. yield of crude product when the imide prepd. by Guareschi's method (*Ann. accad. sci. Torino* 36, 443 (1900–1)) from $PhCH_2COMe$, $CNCH_3CO_2Et$, and alc. NH_3 is heated under a reflux with 400 cc. concd. H_2SO_4 with frequent shaking until evolution of gas ceased and soln. took place, then dilg. with 150 cc. H_2O and extg. with Et_2O , prisms from C_6H_6 , m. 155–6°, insol. in $NaHCO_3$ sol. in 10% hot NaOH and pptd. unchanged by acid; the Ag, Hg°, Pb, Cu°, Cr, Al, Fe°, and Fe'' salts readily form in the cold from the NH_4 salt; the Ba and Ca salts are sol. both in the cold and on boiling; oxidation with acid or alk. $KMnO_4$ yields o - $C_6H_4(CO_2H)_2$, m. 203°, identified

by the fluorescein test and analysis: *semicarbazone*, needles from alc., m. 221°. *ac-1-Keto-ethyltetrahydronaphthyl-3-acetic acid*, obtained like A by hydrolyzing the pure imide prep'd. from PhCH_2COEt , prisms from C_6H_6 and light petroleum, m. 79°; its metallic salts are like those of A; oxidation in acid soln. yields $\text{o-C}_6\text{H}_4(\text{CO}_2\text{H})_2$; *semicarbazone*, needles from EtOH, m. 210°. *3,5-Dicyano-2,6-diketo-4-cyclohexenyl-methyl-4-methylpiperidine* (B), obtained in 12-g. yield of crude product when 13.8 g. cyclohexenylacetone (prep'd. by the method of Wallach, *C. A.* 7, 1002) is condensed with $\text{CNCH}_2\text{CO}_2\text{Et}$ and alc. NH_3 , needles from alc., sinter and darken 190°, m. 202° (decompn.). *1-Keto-3-methyloctahydronaphthyl-3-acetic acid*, obtained in 25% yield when pure B is refluxed with concd. H_2SO_4 , crystals from Et₂O, m. 90°; the metallic salts resemble those of A; oxidation in acid soln. yields $\text{o-C}_6\text{H}_4(\text{CO}_2\text{H})_2$; *semicarbazone*, needles from hot alc., m. 209–10° (decompn.). When 0.5 cc. 50% KOH is added to 8.4 g. $\text{CNCH}_2\text{CONH}_2$ and 6 g. PhCH_2CHO in 50 cc. H_2O and enough alc. for soln., and the crystals which sep. in 24 hrs. are extd. with hot alc., there is left a small quantity of the α,α' -dicyano- β -benzylglutaric diamide $\text{PhCH}_2\text{CH}(\text{CN})\text{CONH}_2$, needles, m. 245°, and on cooling were obtained needles, m. 204°, apparently formed by the condensation of $\text{CNCH}_2\text{CONH}_2$ and PhCH_2CHO in equimol. proportions. H. GILMAN.

The action of the chlorides of sulfur on substituted ethylenes. The action of propylene on sulfur monochloride and the synthesis of β,β' -dichlorodipropyl sulfide, SAMUEL COFFEY. University Coll., Nottingham. *J. Chem. Soc.* 119, 94–8(1921).—Preliminary report on the action of S_2Cl_2 and SCl_2 on substituted ethylenes. (For a more complete study of related work by Conant, Hartsborn, and Richardson, cf. *C. A.* 14, 1677–8). When about 20 g. $\text{MeCH}:\text{CH}_2$ is passed through 15 g. S_2Cl_2 kept below 50° and the dark brown semisolid is extd. with CHCl_3 and then distd., much HCl is evolved, a black tar of more than 25 g. remains, and 5 g. of a red oil, b_{10-12} 113–20°, apparently of β,β' -dichlorodipropyl disulfide, is obtained; it is vigorously oxidized by cold concd. HNO_3 , yielding after boiling with BaCO_3 , a little BaSO_4 , and barium chloropropanesulfonate, pearly plates from 75% hot alc., sparingly sol. in alc., but readily sol. in cold H_2O . β,β' -Dihydroxydipropyl sulfide (A), obtained in 80% yield by gradually adding 12 g. $\text{MeCH}(\text{OH})\text{CH}_2\text{Cl}$ to 37 g. crystd. Na_2S in H_2O , heating on the H_2O bath for 1.5 hr., acidifying with HCl , and cong. the alc. ext. of the residue in vacuum, non-volatile, pale-yellow viscous liquid, sol. in H_2O or alc., and heavier than H_2O . β,β' -Dichlorodipropyl sulfide, obtained in 7-g. yield from 9 g. of A and 70 cc. concd. HCl , colorless oil, b_{25} 122° (liquid at –8°), with properties similar to those of $(\text{ClCH}_2\text{CH}_2)_2\text{S}$ but has no apparent vesicant action, is quant. converted to A by alc. KOH, and is completely decompd. by heating at 100° with concd. HNO_3 , giving H_2SO_4 and a compound, m. 100–2° (apparently the corresponding sulfone). H. GILMAN.

2,4,6-Trinitrotolylmethylnitroamine. OSCAR L. BRADY AND WM. H. GIBSON. *J. Chem. Soc.* 119, 98–104(1921).—2,4,6-Trinitrotolylmethylnitroamine (A) (Blanksma, *Rec. trav. chim.* 21, 327(1902)) was prep'd. by nitrating 2,4,6-trinitromethyl-*m*-toluidine, which was obtained by the action of MeNH_2 on 2,4,6-trinitro-*m*-tolyl Me ether and is now prep'd. from 2,3,4-(NO_2)₃ $\text{C}_6\text{H}_2\text{Me}$ (B) and the 3,4,6-compd. (C). In B and C one of the NO_2 groups is mobile and Hepp (*Ann.* 215, 344(1882)) showed that in C the group was in the 3-position. Here the NO_2 group was displaced by treatment with amines. When C is treated with NH_3 the dinitrotoluidine obtained is identical with the nitration product of *m*- $\text{MeC}_6\text{H}_4\text{NHAc}$ (Cook and Brady, *C. A.* 14, 2915) and the synthesis of A from C confirms the fact that the NO_2 group in the 3-position is the mobile group in the compd. B and C follow Meldola's rule (*C. A.* 3, 2680) for the mobility of groups in negatively substituted C_6H_4 derivs. With MeNH_2 or Me_2NH the corresponding dinitromethyl-*m*-toluidines and dinitrodipropyl-*m*-toluidines are formed, all of which give A on nitration. B and C were prep'd. according to Hepp's method

(*loc. cit.*). B was sepd. from C by crystn. from CS_2 but a more convenient method of prepn. and sepn. was found. A mixt. of 180 cc. HNO_3 (d. 1.42) and 340 cc. 98% H_2SO_4 was added in small portions to 225 g. $m\text{-NO}_2\text{C}_6\text{H}_4\text{Me}$ at 50° , then warmed to 100° , kept at 100° for 30 min. with frequent shaking, cooled to 50° and sepd. The oil was added slowly to 180 cc. HNO_3 (d. 1.5) and 410 cc. 98% H_2SO_4 , warmed to 70° , kept at that temp. for 30 min. with shaking, heated cautiously to 100° and heated for 1 hr. The oil was sepd. hot, run into cold H_2O and steam was injected until the product was acid-free. On cooling, a paste was obtained which was dissolved in boiling alc. (100 cc. of 95% alc. to 12 g. of the mixt.), cooled to 50° and seeded with C. Sandy crystals sepd. The filtrate was treated with H_2O and the solid which sepd. was filtered, dissolved in boiling glacial AcOH . A small amt. of H_2O was added and a seed of B. The product obtained was filtered off rapidly. 2 portions of 235 g. $m\text{-NO}_2\text{C}_6\text{H}_4\text{Me}$ were nitrated. 620 g. mixed B and C were obtained (84%). Three crystals from alc. and 3 from AcOH followed by 1 crystn. of the combined crops from alc. and from AcOH and alc., resp., gave 200 g. pure C and 100 g. pure B. 2,4-Dinitromethyl-m-toluidine (D) was prepd. by treating 20 g. B in 250 cc. hot alc. and 7 g. MeNH_2HCl in H_2O with 12 cc. NH_4OH (d. 0.88). The liquid darkened as the NH_4OH was added but it turned rapidly to a clear orange color. The mixt. was then boiled for a few mins., cooled, and H_2O was added cautiously until crystn. began. The solid was washed to remove NH_4Cl , crystd. from alc. and the D sepd. as long flat crystals m. 81° . They are readily sol. in hot and sparingly sol. in cold alc. 4,6-Dinitromethyl-m-toluidine (E), prepd. as in the case of D, crystd. from boiling alc. in yellow needles m. 173° (vide Wurster and Rideal, *Ber.* 12, 1800(1879)). 2,4-Dinitrotolymethyl-m-toluidine (F), prepd. by treating B in 250 cc. boiling alc. with 9 g. $\text{Me}_2\text{NH}\cdot\text{HCl}$ and 12 cc. NH_4OH , dig. with 2-3 vols. of H_2O and extg. with Et_2O , is an orange noncryst. product. When 10 g. C in 100 cc. boiling alc. were treated with 4.5 g. $\text{Me}_2\text{NH}\cdot\text{HCl}$ and 6 cc. NH_4OH 2,4,5-(NO_2) $_3\text{MeC}_6\text{H}_3\text{NMe}_2$ sepd. from the cooled mixt. (*Ber.* 12, 1800(1879)). Crude $\text{MeNH}_2\cdot\text{HCl}$ containing Me_2NH and a mixt. of B and C gave a product, 40 g. of which were added in small portions to 100 cc. HNO_3 (d. 1.5) at 50° , heated until red fumes were no longer evolved; H_2O was added to the cold mixt. and A sepd. as an oil which solidified and, when washed and crystd. from alc. containing AcOH , sepd. usually as an oil, thus making complications. When 5 g. D were added to 50 cc. HNO_3 (d. 1.42) at 50° , and kept at this temp. for 5 min., from the hot filtrate 4,6-dinitrotolymethyl-nitroamine (H) sepd., yellow plates from Me_2CO , m. 157° . On nitration A was formed. The NO_2 group attached to N was removed by heating H with 0.5 g. PhOH in 20 cc. 80% H_2SO_4 for 30 min. From this mixt. E was obtained. 2,4-Dinitrotolymethyl-nitroamine, prepd. in a similar manner from D, seps. from alc. as pale yellow needles, m. 111° . On further nitration A was formed, but when treated with PhOH and H_2SO_4 2,4,6-trinitromethyl-m-toluidine (J) was obtained and not D as would be expected. 2,4,6-Trinitromethyl-nitrosamine (K), prepd. by treating 6 g. J in 50 cc. glacial AcOH with 30 cc. of a 20% soln. of N_2O_4 in AcOH and gradually adding H_2O with thorough shaking, is a buff granular ppt., m. 120° . 2,4-Dinitrotolymethyl-nitrosamine, colorless needles, m. 65° , and 4,6-dinitrotolymethyl-nitrosamine, brilliant yellow needles, m. 94° , were prepd. from D and E resp. D and E could not be nitrated directly to 2,4,6-trinitromethyl-m-toluidine but this compd. was prepd. by treating 5 g. of the nitroamine with PhOH in 50 cc. 80% H_2SO_4 at 90° for 30 min.

H. B. WILLIAMS

Organic derivatives of tellurium. III. Crystallographic and pharmacological comparison of the α - and β -dimethyltelluronium dihalides. ISABEL ELLIS KNAGGS AND RICHARD H. VERNON. *J. Chem. Soc.* 119, 105-8(1921).— α - or "trans"-Dimethyl-telluronium diiodide was prepd. in the usual manner and crystd. from CHCl_3 or C_6H_6 . Crystallographic data are given. The β - or *cis*-form was prepd. from the β -base and

was recrystd. from MeOH as small black crystals of metallic luster. The 2 forms stand to each other in the same relation as the members of an isomorphous series, but in marked contrast to the similarity in cryst. structure of the α - and β -forms is the totally different physiol. action of the α -halides as compared to the corresponding β -forms. The iodides are insol. in H_2O but the chlorides and bromides were investigated from a pharmacological standpoint. Both compds. when taken into the body are excreted from the lungs as Me_2Te , a substance which exerts little physiol. action apart from its odor. The α -compd. slows and weakens the heart and the blood pressure falls, it stimulates plain muscle, particularly that of the uterus and intestines, to increased activity, though the action on the nervous system was almost negligible. The compd. has the most profound stimulant action on the medulla; it increases blood pressure and increases the depth and rapidity of respiration. Generally before the blood pressure has reached the normal again a second rise occurs due to the liberation of adrenaline from the suprarenal glands, upon which the compd. exerts a unique and sp. action incomparable with that produced by any other reagent. 60 mg. of the β -compd. (to a cat) paralyzed the brain, spinal cord and motor nerves.

H. E. W.

The ethylenic isomerism of ω -bromostyrene. CHARLES DUFRAISS. *Compt. rend.* 172, 67-9(1921).—The prepn. of three isomeric bromostyrenes has been described previously (C. A. 15, 670). Two of these are stereoisomeric ω -bromostyrenes $PhCH:CHBr$, which differ in odor, color and m. p. Sunlight transforms these isomeric forms (designated I and II) into an equil. mixt. of the two. To demonstrate this place a small amt. of I and II in separate test-tubes. In a 3rd test-tube place an equal mixt. of the two. I m. 7° , II at -7° , and the mixt. crysts. only below -20° . After exposure of the three tubes to the sunlight for an hour, all three samples melt at the same temp., $+2^\circ$, showing that an equil. mixt. has been formed, alike in the three cases. In another expt. this transformation is followed by taking m. ps. at frequent intervals. With I the m. p. dropped gradually from 7° to 2° . With II, however, the m. p. fell rapidly from -7° to -20° and then rose to 2° . Contrary to expectation the stable isomer, which is the higher melting, is transformed most rapidly under the influence of light. In semi-darkness I was completely changed to the equil. mixt. in 3 months, while II was unaffected. On account of this change caused by light, care should be taken in prep. the pure isomeric forms.

J. B. BROWN

The action of the alkali metals on ethers. J. DURAND. *Compt. rend.* 172, 70-1 (1921).—It had been noticed that in drying ether with Na, H was evolved even after long standing. Consequently a study was made of the action of Na and Na-K alloy on aliphatic, aromatic and mixed ethers. Et_2O reacted slowly with formation of alcoholate and H gas, but the low b. p. of the ether prevented tests at high temp. With (iso-Am) $_2O$ there was slow action in the cold and vigorous action at the b. p., where the metal was liquid. Anisole, phenetole and veratrole reacted rapidly in the hot, until the reaction mass solidified. $PhCH_2OEt$ behaved similarly. Ph_2O reacted readily with carbonization. K-Na is liquid at ordinary temp., and in general reacted more vigorously, particularly in the cold. The reaction was explained by the following equation; $ROR' + Na = RONa + R'-$. $R'-$, which cannot exist in the free state, then condenses. If the product formed is a phenate, this in turn may be attacked by the metal with formation of resinous bodies. Further studies are to be made on other types of ethers.

J. B. BROWN

The autoxidation of α -bromostyrolene. CHARLES DUFRAISS. *Compt. rend.* 172, 162-5(1921).—Bromostyrolene, contrary to expectation, oxidizes to $PhCOCH_2Br$ and not to $PhCHBrCHO$. This migration of the Br atom in autoxidation has not been recognized before. Demole (*Ber.* 2, 315(1868)) shows that an autoxidation

$\text{CBr}_2\text{CH}_2 \longrightarrow \text{CH}_2\text{BrCOBr}$ and $\text{CClBrCH}_2 \longrightarrow \text{CH}_2\text{BrCOCl}$ and CH_2ClCOBr . In general the halogen migrates in preference to the H atom in this type of oxidation. X and Y being electronegative groups, unsym. compds. $\text{XYC}=\text{C}$ = oxidize readily in the air and $-\text{XC}:\text{CY}-$ compds. do not. Example. $\text{Ph}_2\text{C}:\text{CH}_2$ autoxidizes to Ph_2CO and CH_2O while stilbene does not. The lacrymatory qualities of α -bromostyrene, not noticeable when it is freshly distd., are due to its autoxidation by air to PhCOCH_2Br , a well known lacrymator. Conclusions: (1) The negative groups migrate in preference to H atoms, when migration accompanies autoxidation. (2) Autoxidation of an ethylene linking is most pronounced when the electronegative groups are most unsymmetrical. (3) The autoxidation of α -bromostyrene proves its constitution. (4) The irritating qualities of α -bromostyrene are due to the presence of PhCOCH_2Br .

R. E. SABIN

The variation of rotatory power of tartaric acid. R. DE MALLERMAN. *Compt. rend.* 172, 150-2(1921).—The addition of the salts of H_3BO_3 , H_2SbO_4 , H_2MoO_4 , H_2WO_4 to aq. solns. of *d*-tartaric acid gives compds. with high rotatory power, increasing the rotatory power of the mixed soln. (Darmon, *Compt. rend.* 171, 349(1920)). Addition of the chlorides of Na, Ca, Sr, Ba, and the nitrates of Na, Ca, and Sr, decreases the rotatory power of tartaric acid in aq. soln., while MgCl_2 , ZnCl_2 , and $\text{Ba}(\text{NO}_3)_2$ increase the rotation. The effect of the Na salts is very slight. The bivalent metal salts are in the order of their decreasing power of reducing the rotation power of tartaric acid solns. The dispersion seems to follow a characteristic rule, which applies to the variations caused by the addition of quite a number of metallic salts. Conclusions: For equal concns. the alk. earth metals give the greatest depression. This effect is very large in passing from the alkali metals to Ca. Then it decreases in the order Ca, Sr, Ba, Mg and Zn. It is larger for the chlorides than for the nitrates or the sol. sulfates. The effect increases with the concn. of the salt and the tartaric acid and with the salt-acid ratio but then seems to pass a max. Increase in temp. has the same effect as diln. The dispersion curves are instructive. They indicate that: any curve that cuts the ordinates between two curves has a fixed ratio to them (cf. Darmon, C. A. 6, 2888). The curves for pure tartaric acid agree with this theory. It seems that the same causes det. the variation of the rotation in both cases.

R. E. SABIN

The catalytic decomposition of the chloroacetic acids. J. B. SENDRENS. *Compt. rend.* 172, 155-8(1921).—S. investigates the catalytic decompn. of mono- and trichloroacetic acids with thoria, china clay and animal charcoal (from blood). It was hoped to get $\text{CO}(\text{CH}_2\text{Cl})_2$ in accordance with the general equation $2\text{RCO}_2\text{H} = \text{H}_2\text{O} + \text{CO}_2 + \text{R}_2\text{CO}$. With thoria $\text{CH}_2\text{ClCO}_2\text{H}$ decomp., beginning at 220° to 340° , into CO_2 , CO , HCl , $(\text{CH}_2\text{Cl})_2$ and pptd. C. $\text{CCl}_3\text{CO}_2\text{H}$ breaks up into the gases COCl_2 , CO , and the liquids CHCl_3 , C_2Cl_4 and CCl_4 . China clay reacts similarly to thoria toward mono- and trichloroacetic acid, only at a slightly higher temp. Animal charcoal acts the same to $\text{CH}_2\text{ClCO}_2\text{H}$ as thoria and china clay. $\text{CCl}_3\text{CO}_2\text{H}$ breaks down into CO_2 , CO and small amts. of C_2Cl_4 , C_3Cl_8 , HCl and a fair yield of CHCl_3 according to the reaction $\text{CCl}_3\text{CO}_2\text{H} = \text{CHCl}_3 + \text{CO}_2$. Contrary to expectations chloral does not break down into CHCl_3 and CO with either thoria or animal charcoal.

R. E. SABIN

The two homologs of ethylene sulfide: 1,2-thiopropane and 1,2-thiobutane. MARCEL DELÉPINE AND PIERRE JAFFEUX. *Compt. rend.* 172, 158-60(1921).—The writers have made these compds. to study the characteristics of compds. containing the heterocyclic ring of 2 carbons and one sulfur. These compds. are colorless liquids, mobile, with a strong peculiar odor (not like garlic) similar to ethylene sulfide, insol. in H_2O and miscible in org. solvents. They are very volatile. They are not so re-

active as ethylene sulfide. H_2SO_4 forms a transparent jelly, HCl does not polymerize these compds. but seems to react. HNO_3 oxidizes them. NH_4OH and concd. alkali slowly form viscous substances. Ag , Hg and Pt salts ppt. with them. Mg forms unstable compds. Pyridine turns brown on contact as with ethylene sulfide but does not form a ppt. These compds. have not polymerized on standing six months. *1,2-Thio-propane* (A), $\text{S.CH}_2\text{CHMe}$, b_p 75–77°, d_4^{20} 0.964, n_D^{19} 1.473, RM_{20} 21.97, refraction for S 8.11. The corresponding consts. for *1,2-thiobutane* (B), $\text{S.CH}_2\text{CH}_2\text{Et}$, are 104–105°,

0.944, 1.475 (at 15°), 26.64, 8.16. A was prepd. through the following compds.:

$\text{PROH} \xrightarrow[\text{catalytically}]{-\text{H}_2\text{O}}$ propylene \longrightarrow propyl dihydromide \longrightarrow dithiocyanate $\xrightarrow{\text{Na}_2\text{S}}$ little H_2S

A. Another part has been changed into $\text{MeCHClCH}_2\text{Br}$ and $\text{MeCHBrCH}_2\text{Cl}$ and these into the chlorothiocyanate and dithiocyanate, which on treating with Na_2S containing a little H_2S give A. B was prepd. from BuBr (obtained from BuOH and HBr), one part of which was changed into 1,2-butylene by alc. KOH and then into the dihydromide by Br . Another method consisted in brominating in sunlight according to Reiboul's method (*Compt. rend.* 113, 589(1891)). The $\text{EtCHBrCH}_2\text{Br}$ with 1 mol. thiocyanate gives thiobromothiocyanate and dithiocyanate, which on treating with Na_2S give B. Also in *Bull. soc. chim.* 29, 136–42 (1921).

R. E. SABIN

Synthesis of cyanic acid by oxidation of formamide and oxamic acid. R. Fossé. *Compt. rend.* 172, 160–2(1921).—Oxamic acid is often produced in organic oxidations in the presence of NH_3 , while HCONH_2 is noted more rarely. Oxamic acid is made by oxidizing glycocholl (*Compt. rend.* 79, 808; *Ber. K. K. Ges. Wiss.* 1875; *Z. physiol. Chem.* 25, 325); NH_2 acids, albumin; gelatin (*Sitz. K. pr. Akad. W.* 1903 and *Ber.* 37, 2908, (1904)); glucose, glycerol and alc. acids in NH_3 solns. HCONH_2 is made by the action of KMnO_4 on MeOH and glycerol in the presence of NH_3 ; from CO and NH_3 by the electric spark (*Ber.* 30, 138(1897)) and ultraviolet light (Berthelot and Gaudechon, *C.A.* 4, 2408). Both are converted to urea by KMnO_4 (*Arch. exp. Path. Pharm.* 37, 426 (1896); *Beitr. chem. Physiol. Path.* 6, 481(1905)) or by electrolytic oxidation (*Fichter, C.A.* 7, 52). Halsey oxidized HCONH_2 and oxamic acid, obtaining HOCN as indicated by tests (Fossé, *C.A.* 15, 217). *Cyanic acid synthesis from oxamide.* To 1.14 g. HCONH_2 in 10 cc. concd. NH_4OH add while stirring, 5 g. ground KMnO_4 in small amts. Oxidation requires 15 mins.; vol. of soln. 27 cc. *Urea produced by heating this soln. with NH_4Cl .* Heat one hour under a reflux 2 cc. of this soln. at 95° with NH_4Cl , introducing 7 cc. AcOH and 0.1 cc. xanthylol in MeOH . Yield 0.041 g. dioxanthylurea equiv. to 6.93 g. urea to 100 g. HCONH_2 . A trace only of dioxanthylurea is formed when the above is not heated. Color reactions: To this soln. add AgNO_3 and HNO_3 until only slightly alk.; dry and grind the ppt. with KCl and $(\text{AcO})_2\text{Co}$. On contact with moist air from one's mouth the mixt. becomes intensely blue. Dil. FeCl_3 colors a trituration of the Ag salt with $\text{NH}_4\text{OH.HCl}$ a violet blue. *Cyanic acid synthesis from oxamic acid.* Oxidize $\text{NH}_2\text{COCO}_2\text{NH}_2$ in 10 cc. each of H_2O and NH_4OH with 5 g. KMnO_4 , heating gently. Vol. = 25 cc. *Urea produced by heating this liquid with NH_4Cl .* Yield = 0.0058 g. The dioxanthylurea from 2 cc. of this liquid is equiv. to 1.03 g. for 100 g. of $\text{NH}_2\text{COCO}_2\text{NH}_2$. A trace only of dioxanthylurea is formed when the above is not heated. Color reactions: Ext. a small quantity of the crystals with boiling water, discard the filtrate; the remaining crystals give the two characteristic color reactions.

R. E. SABIN

6-Methylisatin J. BONNEFOY AND JH. MARTINET. *Compt. rend.* 172, 220–1 (1921).—Two methods for prepg. 6-methylisatin (Findeklee, *Ber.* 38, 3542(1905)) from $m\text{-MeC}_6\text{H}_4\text{NH}_2$ are given. (1) Et or Me mesoxalate is condensed with

$m\text{-MeC}_6\text{H}_4\text{NH}_2$ in AcOH, giving ethyl or methyl 6-methyldioxindole-3-carboxylate, *m.* 186°, and 248–50°, resp. By treatment with air these esters are decarboxylated, the dioxindole formed is oxidized, turning the soln. brown and finally changing to the characteristic yellow color of an alkali isatate. Mineral acid will ppt. the free isatin. (2) Di-*m*-tolylthiourea in dil. alc. is treated with KCN and PbCO_3 on a steam bath, forming hydrocyanodi-*m*-tolylcarbodiimide (A), $\text{MeC}_6\text{H}_4\text{NHC}(\text{CN})\text{:NC}_6\text{H}_4\text{Me}$, pale yellow crystals from alc., *m.* 128°. A in dry C_6H_6 is treated for 4 hrs. at 40° with 3 times its wt. of AlCl_3 . The violet-red solution is poured on ice, decanted, dried and crystals of the 6-methylisatin-*m*-toluide, *m.* 65–7°, sol. in alc., C_6H_6 , CS_2 and AcOH, are obtained. On boiling the toluide with dil. HCl, $m\text{-MeC}_6\text{H}_4\text{NH}_2$ is split off, giving 6-methylisatin. The latter in AcOH treated with $\text{PhNHCH}_2\text{CO}_2\text{H}$ gives 6-methyl-3-indole-2-indigo, *m.* 307°, which will color wool and silk but gives only a very pale mauve to cotton.

R. CHESTER ROBERTS

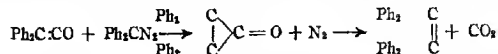
Derivatives of 1,4-diketones and semicarbazide. E. E. BLAISE. *Compt. rend.* 172, 221–3 (1921).—The disemicarbazone of acetylacetone in HCO_2H on a steam bath rearranges when dild. with water to form one mole of $\text{H}_2\text{NCONHNH}_2$ and *N*-carbamido- α,α' -dimethylpyrrole (A), needles from alc., *m.* 245°. Zn and HCl will reduce A to urea and α,α' -dimethylpyrrolidine. B. synthesizes A by hydrolyzing *N*-formylaminodimethylpyrrole with aq. KOH to form *N*-aminodimethylpyrrole, *m.* 52°, *b_p* 109°, which will react with HNCO to give A. B. concludes that 1,4-diketones do not give pyridazine derivs. with PhNHNH_2 alone. With acyclic diketones a mixt. of pyridazines and tetrahydropyridazines is formed rather than the dihydropyridazines. The monosubstituted hydrazines as PhNHNH_2 , AcNHNH_2 , HCONHNH_2 and $\text{NH}_2\text{NHCNH}_2$ form no pyrrole derivs.

R. CHESTER ROBERTS

New general methods for preparing amines from aldehydes and ketones. GEORGES MIGNONAC. *Compt. rend.* 172, 223–6 (1921).—A soln. of dry NH_3 in abs. alc. (7–8 per 100) is used to dissolve the aldehydes or ketone, enough NH_3 being used to form the imine, i. e., 1 mol. NH_3 to 1 mol. aldehyde. Finely divided Ni is added as the catalyst and the mixt. vigorously shaken in an atm. of H_2 under about atm. pressure. The temp. is kept at 15–20° and hydrogenation takes place regularly. The reaction is stopped when the absorption becomes feeble. After sepn. of the catalyst, the amine is isolated by the usual methods. The quantity of amine obtained corresponds to the fixed H. M. prepd. the following amines by this method: ethyl, diethyl, butyl, di-n-butyl, heptyl, benzyl, benzalbenzyl and *p*-ethylbenzyl from aldehydes and isopropyl, diisopropyl, octyl, cyclohexyl, α -phenylethyl, α -phenylpropylamines and amino-6-methylheptene from ketones. M. gives a short discussion of the mechanism of this reaction.

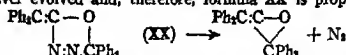
R. CHESTER ROBERTS

Ketenes and aliphatic diazo compounds. H. STAUDINGER AND T. REBER. *Zurich. Helvetica Chim. Acta* 4, 3–23 (1921); cf. *C. A.* 14, 3424.—An investigation of the interaction of ketenes and a series of aliphatic diazo compds. was made to det. the steps in the reaction and also in the hope of prepg. ketone derivs. of the unknown cyclopropanone series which were of interest because of the ring strain; such compds. are likely to decomp. with the formation of ethylene derivs. The previous statement (cf. Staud-



inger, *Die Ketene* p. 94) that $\text{Ph}_2\text{C:CO}$ (A) and $\text{N}_2\text{CHCO}_2\text{Et}$ (B) react to form the cyclopropanonecarboxylic acid ester (III) is corrected as it is found that it is a much more complicated reaction which takes place with the formation of I or II. Another type of addition is where B attaches to the CO group of A (cf. *C. A.* 14, 2490), yielding a compd. of the type V or VI, which decomps. into an ethylene oxide deriv. In

tained, CO_2 was never evolved and, therefore, formula XX is proposed. BzPhCN_2 ,



unlike the others, reacts very slowly with A; the product will be investigated later. To 43.6 g. A in 90 cc. abs. Et_2O , 27 g. B in 90 cc. abs. Et_2O are added during 1 hr. at $15-20^\circ$ in a CO_2 atm.; after 12-20 hrs. the crystals C are sepd. and washed with abs. Et_2O ; from the mother liquors several crops of crystals are obtained on evapn. and finally a resin seps. (D). C is a mixt. of IV and VII, from which IV is sepd. by warming with dil. Na_2CO_3 , forming a Na salt, filtering and treating repeatedly with H_2O , which dissolves the salt; this operation is repeated several times with the insol. residue; the aq. soln. on acidifying yields almost pure IV; the insol. portion is impure VII. IV is readily sol. in PhH, EtOH or glacial AcOH; recrystd. from Et_2O it m. 140° ; it is very stable, remaining unchanged on treatment with dil. acids or alkalis; when heated under pressure with concd. HCl a resin is formed; on warming with 50% H_2SO_4 a blue color is formed; concd. H_2SO_4 gives first a red, then green followed by decompn.; FeCl_3 in MeOH gives a deep blue color which is used in testing for traces; the Na salt and Me_2SO do not form an ether; no characteristic compds. were formed with SOCl_2 or AcCl ; reaction takes place in the presence of NaOAc with $\text{N}_2\text{H}_4\text{CONH}_2$, HCl, PhN_2H_2 , and $p\text{-NO}_2\text{C}_6\text{H}_4\text{N}_2\text{H}_2$, but only with the last was a small quant. of cryst. compd. obtained; boiling with NaOEt in EtOH yields an acid of unknown constitution, m. 126° ; oxidation does not yield cryst. compds.; reduction with Pt and H yields a series of resinous products; one reduction product of unknown constitution, m. 108° ; when treated with 2 N Br in CS_2 a cryst. compd. (IX) is obtained, m. 110° . VII was recrystd. from Et_2O + petr. ether until FeCl_3 showed no blue color; it is readily sol. in Et_2O , EtOH or PhH, insol. in petr. ether, m. 124° ; when heated it decomp. into $\text{Ph}_2\text{C}:\text{CH}:\text{CO}_2\text{H}$; heated with concd. H_2SO_4 the colors yellow, red, violet, brown are formed; 50% H_2SO_4 gives light blue; CrO_3 or $\text{Na}_2\text{Cr}_2\text{O}_7$ in Ac_2O oxidizes VII to Ph_2CO ; KMnO_4 oxidizes it when heated; it is stable towards reduction with Pd; heated with concd. KOH Ph_2CO is finally formed; $\text{N}_2\text{H}_4\text{CONH}_2$, PhN_2H_2 and NH_2OH do not react; AcCl and VII heated for several days, extd. with Et_2O , washed with Na_2CO_3 and recrystd. from Et_2O + petr. ether yield the β -lactone of β -benzohydrylidene- β -hydroxy- α -acetoxypropionic acid (XV), m. 111° . XV when heated, then boiled with alkali gives a quant. yield of XI. *Benzohydrylidenepyrotartaric acid*, α -keto- γ,γ -diphenyl- $\Delta^{2,3}$ -propenecarboxylic acid (XI) was prepd. by heating VII with concd. HCl until solidification occurred; recrystd. from dil. EtOH, it m. 207° ; $\text{Na}_2\text{Cr}_2\text{O}_7$, 30% H_2O , Ac_2O or concd. KOH forms Ph_2CO ; there is no reaction with SOCl_2 , PhN_2H_2 or NH_2OH ; $\text{N}_2\text{H}_4\text{CONH}_2$ forms a deriv. of unknown constitution; attempts to prep. $\text{Ph}_2\text{C}:\text{CHCO}_2\text{H}$ with concd. H_2SO_4 were not successful; the Ag salt with EtI in Et_2O forms an *ethyl ester* (XII), recrystd. from dil. EtOH or Et_2O + petr. ether, m. 110° ; when XII in Et_2O is treated with Br in CS_2 and allowed to stand a day, crystals of *ethyl β -benzohydrylidene- α -bromoethylene-oxide-carboxylate* (XVI) sep., recrystd. from Et_2O , m. 117° ; the mother liquors contain XVII; XVI boiled with concd. HCl or HBr, or XI treated with Br yields β -benzohydrylidene- α -bromopyrotartaric acid (XVII), recrystd. from dil. EtOH, m. 224° . *Monoethyl benzohydrylidenebromopyrotartaric acid* (XVIII), from the Ag salt of XVII and EtI in Et_2O , m. 162° . A and $\text{N}_2\text{CHCO}_2\text{Me}$ do not yield satisfactory results and the Et ester is preferable. From the mother liquors of the interaction of A and B, resinous compds. (D) are obtained which on treatment with Na_2CO_3 give an acid of unknown constitution; recrystd. from Et_2O it m. 217° ; on long standing of D a small quantity of a neutral compd., m. 158° , was obtained by extn. with various solvents, which is probably a polymerized product; analysis gave $\text{C}_{15}\text{H}_{10}\text{O}_4$; A and Ph_2CN_2 react to form XX, m. 136° ; it decomp. at $160-70^\circ$ with evolution of N_2 ; alkalis, acids, alc. NaOH or PhN_2H_2

has no action on **XX**. (*p*-MeOC₆H₄)PhCN₂ and **A** in Et₂O form Ph₂C:N:N.CPh(C₆H₄OMe).O(?), yellow crystals from Et₂O, m. 115-6°. PhBzCN₂ and

A were allowed to react in CO₂ for several days, yielding a compd. of unknown constitution containing 2 mols. ketene and 1 mol. diazo compd.; recrystd. from EtQH⁺ and EtOAc, it m. 174°.

N. A. LANGE

The nitrobenzoates of the three cresols. EUGEN HANGGI. Univ. Freiburg. *Helvetica Chim. Acta* 4, 23-5(1921).—The urethans with PhCNO and the nitrobenzoates of the three cresols were prepd. for the identification of the cresols as a preliminary for some work to be published later. In the meantime the properties of these urethans were published by Weehuizen (cf. *C. A.* 13, 708) and were identical with those obtained by H. The nitrobenzoates were prepd. by adding 10 mols. of 10% NaOH soln. with shaking to a mixt. of 1 mol. cresol and 1 mol. NO₂C₆H₄COCl, warming to 30-40° for 15 min. with thorough agitation, filtering, washing, drying and recrystg. from EtOH + H₂O; C and D were recrystd. from Me₂CO + H₂O. *o*-Nitrobenzoate of: *o*-Cresol (**A**), colorless prisms soften 64°, m. 68-9°, readily sol. in boiling AcOH, EtOH, PhH, Me₂CO or CCl₄. *m*-Cresol, colorless prisms soften 56°, m. 58.5-60°, fairly sol. in hot petr. ether, readily sol. in EtOH, PhH or CCl₄. *p*-Cresol, colorless plates, soften 77°, m. 78-9.5°, soly. same as **A**. *m*-Nitrobenzoate of: *o*-Cresol, colorless rhombs which soften 94°, m. 96.5-7.5°, readily sol. in hot AcOH, PhH, Me₂CO or CCl₄, fairly sol. in hot EtOH. *m*-Cresol (**B**) seps. first as an oil which solidifies on standing; colorless rhombs, soften 81.5°, m. 63-4°, readily sol. in hot AcOH, EtOH, PhH or Me₂CO, fairly sol. in petr. ether. *p*-Cresol (**C**), flat prisms, m. 77-8°, with the same soly. as **B**. *p*-Nitrobenzoate of: *o*-Cresol, colorless needles, soften 88.5°, m. 92-3°, with soly. same as **B**. *m*-Cresol, colorless, m. 85-5.5°, with the same soly. as **B**. *p*-Cresol, colorless plates, m. 96.5-7.5°, with the same soly. as **A**.

N. A. LANGE

The absorption spectra of some nitro derivatives of acridine, phenoxazine and thiodiphenylamine. F. KEHRMANN AND HENRI GOLDSTEIN. Univ. Lausanne. *Helvetica Chim. Acta* 4, 26-31(1921).—The investigation was undertaken to ascertain the relation existing between structure and absorption. The NO₂ derivatives were examd. as Na salts in EtOH. The following conclusions were drawn: (a) The depth of color of the alk. solns. increases in the order C:Ph, O:S; if one compares derivs. substituted in the same position, the derivs. of thiodiphenylamine possess the greatest while those of acridine possess the least color; (b) the replacement of NMe by S in the salts studied, causes a further increase in color; (c) if the positions of the NO₂ groups are the same, the absorption spectra of the three series are of an analogous form; (d) the introduction of a NO₂ group in the chromogen para to the ring N increases the color (cf. *C. A.* 13, 3175); (e) the further introduction of NO₂ groups in the *p*-NO₂ compds. decreases the color; (f) the red color of the alk. alc. soln. of *asym*-mono- and diphenylacridine is not as distinct when cold. The substances investigated with a table showing their absorption were the following: 3-nitrodiphenylacridine, 3-nitrophenoxazine, 3-nitrothiodiphenylamine, 3,1(?)-dinitrodiphenylacridine, 3,1-dinitrophenoxazine, 3,1-dinitrothiodiphenylamine, 3,6-dinitrodiphenylacridine, 3,6-dinitrophenoxazine, 3,6-dinitrothiodiphenylamine, 1,3,6-trinitrodiphenylacridine, 1,3,6-trinitrophenoxazine, 1,3,6-trinitrothiodiphenylamine, 1,3,6,8-tetranitrodiphenylacridine, 1,3,6,8-tetranitrophenoxazine, 1,3,6,7-tetranitrophenoxazine, 1,3,7-trinitrophenoxazine, 1,3,5,7-tetranitrophenoxazine, 1,3,6,8-tetranitrodiphenylacridine with a further NO₂ group in each of the two Ph groups, and 1,3-dinitromethylidihydrophenazine.

N. A. LANGE

The isolation of amino alcohols and choline from natural amino acids. P. KARRER, W. KARRER, H. THOMANN, E. HORLACHER AND W. MADER. Univ. Zurich. *Helvetica*

Chim. Acta 4, 76-99(1921).—The natural NH_2 acids as alanine, leucine, phenylalanine, etc., are readily reduced to the corresponding NH_2 alcs. with satisfactory yields. This reduction of the esters of the NH_2 acids may be carried out directly with Na in EtOH, although with poor yields; it is better if the acetylated esters are reduced with Na in EtOH. When optically active material is the starting product, the NH_2 alcs. may still be active; yet there is always an appreciable amount of racemization. While glycine has not been reduced in this manner as yet, it does not seem as if this were impossible and work is being done along this line. Cholines are obtained on methylation of the NH_2 alcs. but with poor yields; so that the compds. described in this paper were prepd. by the reduction of the esters which already contained the Me groups: $\text{Me}_2\text{CHCH}_2\text{CH}(\text{NMe}_2)\text{CO}_2\text{Et} \longrightarrow \text{Me}_2\text{CHCH}_2\text{CH}(\text{NMe}_2)\text{CH}_2\text{OH} \longrightarrow \text{Me}_2\text{CHCH}_2\text{CH}(\text{NMe}_2\text{Cl})\text{CH}_2\text{OH}$. A table is given which shows the similarity of choline (A) leucine-choline (B) and phenylalaninecholine (C) with the usual pptg. reagents. The double salt of A and AuCl_3 crystd. from concd. solns. in yellow needles and from dil. solns. in prisms, m. $243-4^\circ$, $250-2^\circ$, 257° , $267-70^\circ$; the double salt of C with AuCl_3 forms supersatd. solns. readily, from which it crysts. in yellow, lance-shaped aggregates, m. 114.5° ; the salt of B and AuCl_3 m. $98-100^\circ$. The salt of A and PtCl_4 forms yellow, rhombic needles, which readily change into broader monoclinic plates, m. $213-6^\circ$ (other m. ps. reported previously are 225° , $232-3^\circ$, $240-1^\circ$); the salt of B and PtCl_4 forms needles or rhombic plates resembling the salt of A and PtCl_4 , gradually changing into 6-sided plates and prisms, m. $211-3^\circ$. The PtCl_4 salt of C resembles A and PtCl_4 , m. 217° ; it is probably monoclinic but approaches closely rhombic symmetry. The crystallographic measurements of some of these double salts are given in detail with photographs of the crystals. A, B and C are pptd. with KI from solns. as periodides, but the reaction cannot be used for differentiation. A, B and C treated with alloxan and the H_2O evapd. give red residues which turn violet on treatment with alkali, showing that the usual test for the detection of A is given also by at least two other similar compds. All the tests so far described would not make it possible to identify with ease B and C in the presence of A and the results reported in the literature are, therefore, of doubtful character and this probably explains the discrepancy in m. p. previously reported. An accurate identification of A, B and C is possible only by: (a) analysis of the Pt or Au double salt, (b) an accurate crystallographic examn. of the Pt salt, the salt of A being monoclinic, (c) the m. p. of the Au double salts. The pharmacological investigation which is as yet uncompleted will show if they are identical with certain "hormones;" thus far it has been found that B has a very slight action on uterus contraction whereas C has an extraordinary activity; the slight action of A on uterus contraction is increased by acetylation; the activity of B is increased in the same manner; these results show that the usual biological test for choline is not specific. Since it is known that not only esters but also amides of carboxylic acids are readily reduced to alcs., it is probable that egg albumin which is composed of an acid amide complex may readily yield NH_2 alcs. on reduction; egg albumin was hydrolyzed, esterified, acetylated and then reduced; it was found to yield a variety of NH_2 alcohols; these results are to be published later. *l*-Leucinol (*l*-isobutyl-1-amino-ethanol-2) (D) was prepd. by slowly adding 70 g. acetylleucine Et ester (cf. *Ber.* 34, 449(1901)) in EtOH to 60 g. Na, boiling 4 hrs. and adding enough EtOH to dissolve all of the Na then 200 cc. H_2O , removing the EtOH *in vacuo*, extg. with Et_2O , evapg. and fractionating the residue; D is obtained in 20% yield at $194-200^\circ$ as an oil miscible with H_2O , d. 0.897; $[\alpha]_D = -1.94^\circ$; since the ester of *l*-leucine is *d*-rotatory, racemization has taken place and it is probable that pure *l*-leucinol would have a sp. rotation greater than the value observed by K.; the hydrochloride of D, prepd. by adding HCl in Et_2O to D in Et_2O is *l*-rotatory, forming white plates, which are readily sol. in H_2O or EtOH

and m. 148–50°. 1.5 parts of D, 2 parts of CS₂ and 0.6 part of KOH were warmed for 2 hrs.; on cooling the crystals of Me₂CHCH₂CH(NHCS₂K)CH₂OH (E) which sep. were washed with EtOH and then recrystd. from EtOH; E is very sensitive to CO₂ and H₂O. *l*-Isobutyl-1-ethan-2-ol-1-trimethylammonium iodide (F), Me₂CHCH₂CH(NMe₃I)·CH₂OH, was prepd. by warming for 2 hrs. 3 g. D, 10 g. MeOH and 4 g. MeI, cooling, adding 1.5 g. KOH, boiling 0.5 hr., adding 4 g. MeI and repeating the operations two times; the KI is removed by filtering, the soln. evapd. to dryness, the residue extd. with EtOH; and the latter slowly evapd., leaving a residue which gradually crysts.; F recrystd. from EtOH-Et₂O, is readily sol. in H₂O and m. 138–9°. *N*-Dimethylleucine ethyl ester (G) was prepd. by adding 50 g. *l*-α-bromoisocaproic acid to 250 g. 25% Me₃NH soln. with cooling and allowing the reaction to proceed for 8 days, distg. to dryness *in vacuo*, extg. with 400 cc. abs. EtOH, adding HCl gas during 6 hrs., removing the EtOH *in vacuo*, dissolving the residue in H₂O, and adding Et₂O and NaOH soln., G was distd. from the Et₂O at 195–9°. *N*-Dimethylleucine (H) was obtained by heating G with 8 parts H₂O in sealed tubes at 120–30° for 6 hrs., filtering, and evapg. the filtrate; the residue extd. with abs. EtOH yields white crystals on the addition of abs. Et₂O, readily sol. in H₂O or EtOH, *l*-rotatory and m. 185°. *N*-Dimethylleucinol (I) was prepd. by slowly adding 16 g. G in 60 cc. abs. EtOH to 16 g. Na at 140–50°, keeping at this temp. for 2 hrs., adding more abs. EtOH until all the Na was dissolved and then pouring into cold H₂O; the EtOH was removed by evapn. and the aq. soln. extd. with Et₂O; on distn. G was obtained at 192–5°. F is best obtained by adding MeI to I in abs. EtOH; Et₂O is added and the crysts. recrystd. from abs. EtOH. The ammonium base of leucinolcholine, (J), Me₂CHCH₂CH(NMe₃OH)CH₂OH, was prepd. by adding 6 g. of Ag₂O to 4.5 g. F in 50 cc. EtOH + 1 cc. H₂O, shaking the mixt. 6 hrs., filtering and evapg. *in vacuo*; the residue is a viscous liquid which does not cryst.; J with concd. aq. picric acid forms a *picrate*; washed with H₂O it m. 136°; when MeCl is passed into I in abs. EtOH white crystals of a *chloride* are formed, m. 173°. *N*-Dimethylphenylalanine Ethyl ester (K) was prepd. by adding 200 g. 33% aq. Me₃NH to 50 g. α-bromo-β-phenylpropionic acid (cf. Ber. 37, 3062(1904)), evapg. to dryness *in vacuo* at 50°, suspending in abs. EtOH, adding dry HCl for 8 hrs., heating 2 hrs. longer and then evapg. to dryness *in vacuo* at 40–50°; the residue was dissolved in H₂O, made alk. with NaOH, extd. with Et₂O and distd. under 8 mm. at 130–4°; a 50% yield of a viscous, colorless oil was obtained. *N*-Dimethylphenylalaninol (L) was prepd. by reduction of K in abs. EtOH with Na; the mixt. was heated 3–4 hrs. at 180° and more EtOH added to dissolve the excess Na, H₂O added, the EtOH evapd., extd. with Et₂O, dried over Na₂SO₄ and vacuum distd.; it b₁₁ 151°. The iodide and chloride of phenylalaninecholine, PhCH₂CH(NMe₃X)CH₂OH were prepd. by adding the Me halide to L in abs. EtOH; the iodide m. 200°, the chloride m. 194°; both are sol. in H₂O. Phenylalanine Et ester was reduced to phenylalaninol (M) in the usual manner at 160°, poured into H₂O, evapd. to a small vol. *in vacuo*, extd. with Et₂O, dried with Na₂SO₄ and distd. under 2–3 mm. at 110–30°; it was purified by conversion to the *hydrochloride* with HCl in EtOH, addition of Et₂O, cooling and filtering; it is readily sol. in EtOH or H₂O and m. 128°. *dl*-Alaninol (N), CH₃CH(NH₂)CH₂OH was prepd. by acetylation of *dl*-alanine ester with Ac₂O and then reduction with Na in EtOH; after heating 2 hrs. more EtOH was added, H₂O added, the EtOH evapd. and then extd. 15 times with Et₂O; after drying the soln. it was distd., b. 173–6°; N has a basic odor, is readily sol. in H₂O, EtOH or Et₂O. Casein (O) was hydrolyzed in the usual manner, esterified (cf. Z. physiol. Chem. 33, 151(1901)), acetylated and then reduced as above; from 500 g. O, 150 g. acetylated NH₂ acid esters were obtained which yielded 20 g. of NH₂ alcs.; these were sepd. into fractions (a) b₁₀₀ 190°, (b) b₁₁ 140–90°, (c) b₁₄ 190–235°; while the components of these fractions were not identified, it is suggested that they are

probably (a) colamine, alaninol, valinol and some leucinols, (b) leucinols, phenyl-ethylalaninol, (c)? The method of isolation was such that NH_3 alics. containing also an acid group would not be present and, therefore, the reduction product of tyrosine would be absent.

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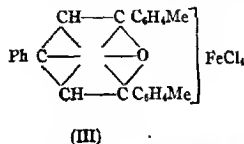
Pyrylium compounds. VIII. WALTHER DILTHER, *et al.* *J. prakt. Chem.* 101, 177–206 (1921); cf. *C. A.* 14, 2641.—Pyrylium salts can be prepd. by the condensation of 1,5-diketones, or of (1) $\text{MeCOR} + \text{RCH:CHCOR}$; (2) $\text{MeCOR} + \text{RCHO}$, and (3) $\text{RCOCH}_2\text{CHRCH}_2\text{COR}$. Ac_2O was used as the condensing agent, and FeCl_3 as oxidizing agent. An average yield of 30% of the Fe salt was obtained. Pyrylium salts react with NH_3 in the cold giving the corresponding $\text{C}_4\text{H}_5\text{N}$ derivs. Use is made of this property for the detn. of constitution, since benzopyrylium and xanthopyrylium salts do not similarly give the corresponding $\text{C}_4\text{H}_5\text{N}$ or acridine derivs. Although many arylated pyrylium salts have been prepd., great difficulty has been met in isolating the free bases, since only colorless substances called pseudo bases were obtained. These compds. form semicarbazones, give deep colored solns. with alkalis + alc., and decomp. with KMnO_4 as follows: $\text{RC(OH)=CHCR} \rightleftharpoons \text{CHCR} \rightleftharpoons \text{CHCOR}$. From their properties it is concluded that these pseudo bases are simply the enolic forms of unsatd. 1,5-diketones. Benzopyranol and α -hydroxychalcone are not satd. but steric isomers represented by (I) and (II). I is the non-salt-forming hydroxychalcone, and



II the pseudo base derived from I by the action of concd. H_2SO_4 . The fact that enolic unsatd. aromatic 1,5-diketones give deep colored solns. with alkalis is significant with respect to the constitution and cause of color of numerous xanthane dyes. On reduction, however, with $\text{H} + \text{Pd}$, the pseudo bases behave like ketones, giving amorphous substances of pinacol nature. Thus in the triphenylpyrylium series a product having the properties of 2,4,6-triphenylpyran is obtained, which is regarded as the parent substance of "triphenylpyran dye," which results on the introduction into the mol. of an auxochrome group, and oxidation. A nomenclature for the anhydro bases is suggested, according to which the simplest *p*-quinopyrone deriv.,

$\text{HC:CH.O.C}(\text{C}_6\text{H}_4\text{:O})\text{CH:CH}$, which occurs in 2 isomeric forms, is termed 2-*p*-clarone,

and to that for the diphenylquinopyrone, $\text{HC:CPh.O.C}(\text{C}_6\text{H}_4\text{:O})\text{CH:CPh}$, the term 2-violone is given. α,ϵ -Di-*p*-tolyl- γ -phenyl- α,ϵ -diketopentane, $(\text{C}_6\text{H}_4\text{COCH}_2)_2\text{CHPh}$, prepd. by warming $\text{BzH} + 1$ mol. $\text{AcC}_6\text{H}_4\text{Me}$ in alkali + alc., m. 115° , gives a colorless soln. with concd. H_2SO_4 , which after several hrs. becomes yellow with green fluorescence; *disemicarbazone* (from 0.5 g. diketone in $\text{C}_6\text{H}_5\text{N}$ and 0.5 g. $\text{H}_2\text{NCONHNH}_2\cdot\text{HCl}$ after standing for 3 days), crystals m. $237-8^\circ$. 2,6-Di-*p*-tolyl-4-phenylpyrylium-*erric chloride* (III), was obtained in quant. yield from BzH and PhAc at 0° , brownish yellow crystals from $\text{AcMe} + \text{Et}_2\text{O}$, m. 258° ; it is decompd. by Na_2CO_3 giving the

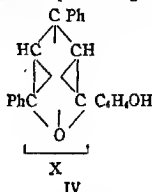
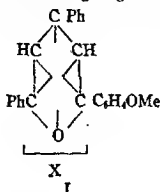


pseudo base, α,ϵ -di-*p*-tolyl- γ -phenyl- α -hydroxy- ϵ -keto- α,γ -pentadiene, $\text{MeC}_6\text{H}_4\text{C(OH):}$.

CHCPh:CHCOC₆H₄Me, crystals from alc. + Et₂O, m. 101°, sol. in Et₂O, gives a greenish fluorescence with concd. H₂SO₄ and a deep red soln. with alkali + alc.; *di-semicarbazone*, m. 214-5°; *picrate*, yellowish red prisms from AcOH, m. 260° (decompn.); *perchlorate*, golden prisms from AcOH, m. 274-5°. The unsym. *tolylpyrylium-ferric chloride* can be prepd. either by condensation of BzMe + PhCH:CHCOC₆H₄Me or of PhCH:CHBz + AcC₆H₄Me, crystals from AcMe + Et₂O, m. 260°, gives yellowish green aq. solns., and on standing for 10 days in an excess of aq. AcONa gave the pseudo base α,γ -diphenyl- ϵ -p-tolyl- α -hydroxy- ϵ -keto- α,γ -pentadiene, PhC(OH):CHCPh:CHCOC₆H₄Me, yellow needles m. 105°, sol. in concd. H₂SO₄ with green fluorescence and in alkali with yellowish red color; on boiling with NaOH in alc. it decomps., giving AcPh, *p*-MeC₆H₄COCO₂H and BzOH, showing that it has the above structure; *picrate*, orange crystals, m. 245-6°; *zinc chloride double salt*, orange crystals, m. 253° (decompn.). 15 g. of *p*-acetylbiophenyl were obtained from 20 g. Ph₂ prepd. according to the method of Willgerodt (cf. C. A. 4, 2283); it was identical with the product similarly obtained by Adams (cf. Ann. chim. [6] 15, 255) who, as well as W., ascribed to the Ac the *m*-position. By gradually adding 8 g. of powdered AlCl₃ to a mixt. of 5 g. Ph₂ and 7 g. AcCl in 25 g. CS₂ diacetylbiophenyl was obtained, leaves from C₆H₆, m. 189°; benzalacetylbiophenyl, prepd. by adding a few drops of 50% KOH to a mixt. of 2 g. PhC₆H₄Ac and 1.2 g. BzH in 60 cc. hot alc. and warming for 10 mins., m. 156°, bright yellow leaves from C₆H₆ (yield 1.7 g.); anisalacetylbiophenyl, similarly prepd., m. 140°, yellow prisms from alc., gives a deep-orange soln. with concd. H₂SO₄; cinnamylacetylbiophenyl, yelow needles from C₆H₆, m. 160°, gives a violet soln. with concd. H₂SO₄. 2-Diphenyl-4,6-diphenylpyrylium-ferric chloride, obtained in 2-g. yield from 2 g. PhC₆H₄Ac and PhCH:CHBz in 12 cc. Ac₂O and FeCl₃ in AcOH, m. 248°, brownish red crystals from AcMe + C₆H₆, easily hydrolyzed by warm H₂O, and is converted by dil. AcONa into the pseudo base *p*-PhC₆H₄C(OH):CHCPh:CHBz, colorless needles from Et₂O, m. 133°, gives greenish yellow, orange-red and red solns. with concd. H₂SO₄, AcOH and alc. KOH, resp.; *disemicarbazone*, small needles from C₆H₅N + alc., m. 218°; *picrate*, red needles from AcOH, m. 222° (previously darkening); *perchlorate*, yellow needles from AcMe + Et₂O, m. 236°; *perbromide*, red needles, m. 228-30°. Benzal-*p*-chloroacetophenone (28 g.) was obtained by adding 20 g. *p*-ClC₆H₄Ac + 22 g. BzH in 50 cc. MeOH to NaOEt in alc. at 5° (the temp. rose to 45°, and the mixt. nearly solidified), hexagonal polygons from Et₂O or CHCl₃, m. 101°; on oxidation it gave *p*-ClC₆H₄CO₂H and BzOH. 2,6-Di-[*p*-chlorophenyl]-4-phenylpyrylium-ferric chloride, prepd. from PhCH:CHCOC₆H₄Cl and AcPh, m. 292°, yellowish red needles from AcMe + C₆H₆; α,ϵ -di-[*p*-chlorophenyl]- γ -phenyl- α -hydroxy- ϵ -keto- α,γ -pentadiene, needles from dil. AcMe, m. 118°, gives greenish fluorescent solns. with both AcOH and concd. H₂SO₄, and violet-red with alkalis; *picrate*; *zinc chloride double salt*, m. 295°. α -*p*-Chlorophenyl- γ,δ,ϵ -triphenyl- α,ϵ -diketopentane, *p*-ClC₆H₄COCH:CHPhCHPhBz, from 4 g. PhCH:CHCOC₆H₄Cl in NaOH added to a hot soln. of 2.4 g. BzCH₂Ph and 0.8 g. Na in 15 cc. alc., prisms from alc., m. 231°. Benzal-*p*-bromoacetophenone (A), PhCH:CHCOC₆H₄Br, from BzH and *p*-BrC₆H₄Ac, m. 104-5°, prisms from ligroin, gives at first a reddish, and finally a yellow soln. with concd. H₂SO₄. Both AcPh + A, and *p*-BrC₆H₄Ac + PhCH:CHBz yielded the same *p*-bromopyrylium-ferric salt, yellowish brown crystals m. 279-80°; pseudo base, greenish yellow needles, m. 103-4°. 2- α -Naphthyl-4,6-diphenylpyrylium-ferric salt, prepd. from PhCH:CHBz, AcC₆H₅, and FeCl₃ in Ac₂O, reddish crystals from AcMe + Et₂O; the corresponding β -naphthyl derivative m. 264°. By boiling for 30 mins. 2 g. PhCH:CHBz and 1.7 g. *p*-AcNH₂C₆H₄Ac with 1-2 g. ZnCl₂ in 10 cc. Ac₂O, allowing the mixt. to stand, removing most of the ZnCl₂ with H₂O, extg. with dil. acid, and finally pptg. with Na₂CO₃, acetyl-

violonimine, PhC:CHC(OH)(C₆H₄NHAc).O.CPh:CH, was prepd., prisms m. 157-8°;

picrate, fine dark red needles, m. 242°; *picrolonate*, reddish, lustrous rosettes from AcOH, m. 233–4° (decompn.). On boiling the Ac deriv. with HCl, and adding to the bluish violet soln. picric acid in alc., *violonimine picrale* sepd., wart-like aggregates of crystals, soften 240°, m. 273° (decompn.), gives in alc. a violet-red soln. without fluorescence. *m*-Substituted pyrylium salts. W. DULTHEY AND CHR. BLOSS. *Ibid* 207–12.—Pyrylium salts having a *p*-OH in the Ph group do not yield with dil. alkalis the corresponding pseudo bases, but give instead deep colored anhydro bases, clarones. This fact led to the study of the influence of an open OH in the *m*-position. *m*-MeOC₆H₄Ac condenses with PhCH:CHBz giving I. This salt would be expected to give the pseudo



base, PhC(OH):CHCPh:CHCOC₆H₄OMe (II), but unlike those previously known it gives no fluorescence with 75% H₂SO₄, only little with 95% acid, and requires H₂SO₄ containing 40% anhydride to give a strong fluorescence. When heated in a sealed tube with HCl it is demethylated, giving PhC(OH):CHCPhCHCOC₆H₄OH (III). Both II and III give *N*-disemicarbazones. The properties of IV agree closely with those of the corresponding *p*-deriv. The salt of III with dil. alkalis does not give a stable, colored anhydro base like the *γ*-derivs. However, when dil. NaHCO₃ is cautiously added to the HCl salt in 70% alc. a violet color is formed, which rapidly disappears. It is supposed that an unstable, unsatd. intermediate compd. is formed of the nature of CPh. *2,4*-Diphenyl-6-*m*-methoxyphenylpyrylium-feric chloride (I), from equimol. amts. of *m*-MeOC₆H₄Ac + PhCH:CHBz, prismatic tablets m. 205°, which on standing for a few days in AcONa gave *α,γ*-diphenyl-*ε*-*m*-methoxyphenyl-*α*-hydroxy-*ε*-keto-*α,γ*-pentadiene (II), yellow needles from MeOH, m. 114–5°; *picrate*, golden needles, m. 176°; *acid chloride*, yellow needles, sinter 130°, m. 180°; *disemicarbazone*, hexagonal prisms, m. 196–8° (decompn.). On heating for 4–5 hrs. at 150–70°, II loses Me with the formation of *2,4*-diphenyl-6-*m*-hydroxyphenylpyrylium chloride, orange needles from alc. + HCl, m. 210–12°. *α,γ*-Diphenyl-*ε*-*m*-hydroxyphenyl-*α*-hydroxy-*ε*-keto-*α,γ*-pentadiene (III), from the above HCl deriv. + AcONa, colorless needles m. 120°, gives a red soln. with alkalis; *picrate*, orange needles m. 268°; *bromide* yellow needles, m. 271–2°; *perbromide*, orange needles, m. 184–5° (decompn.); *iodide*, orange needles, m. 258–7°; *periodide*, brownish violet tablets, m. 233°; *disemicarbazone*, prisms from alc., m. 209° (decompn.).

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Action of the three isomeric ethylaminobenzoic acids on benzo- and toluquinone. B. LINKER. Vienna. *J. prokl. Chem.* 101, 265–72 (1921).—Alkyl *o*-, *m*- and *p*-H₂NC₆H₄CO₂H derivs. react with C₆H₄O₂ in alc. with the formation of the corresponding mono- and dianilides. If the reaction be carried on in dil. AcOH, the mono derivs. only are formed. Under both conditions C₆H₅MeO₂ gave only monoanilides. *2,5*-Di-[*N*-ethyl-*o*-aminobenzoic acid]-1,4-benzoquinone, C₆H₄O₂(NEtC₆H₄CO₂H)₂, prepd. by boiling 6.48 g. C₆H₄O₂ with 6.6 g. *o*-H₂NC₆H₄CO₂H in 95% alc. for several hrs., and allowing the mixt. to stand 24 hrs., chars without m., brown cryst. powder from AcMe, gives a yellow soln. with concd. H₂SO₄; insol. in concd., hut sol. in dil. alkalis. The reaction proceeds in accordance with the equation: 2EtNHC₆H₄CO₂H + 3C₆H₄O₂ = C₆H₄O₂(NEtC₆H₄CO₂H)₂ + 2C₆H₄(OH)₂. Similarly the corresponding *m*-amino- and

p-amino derivatives were prepd., dark brown cryst. powder, and dark red, metallic crystals, resp., from AcMe. Some monoanilides also were formed in the above reactions, and were isolated from the alc. filtrate. By carrying on the reaction in H₂O slightly acidified with AcOH, and then strongly acidifying with AcOH, the monoanilides are formed exclusively; $2\text{C}_6\text{H}_4\text{O}_2 + \text{EtHNC}_6\text{H}_4\text{CO}_2\text{H} = \text{C}_6\text{H}_5\text{O}_2\text{NEtC}_6\text{H}_4\text{CO}_2\text{H} + \text{C}_6\text{H}_5(\text{OH})_2$. These compds. char without melting. 2-[*N*-Ethyl-*o*-aminobenzoic acid]-1,4-benzoquinone, dark brown cryst. powder with violet luster; *m*- and *p*-amino derivatives, dark brown and black cryst. powders, resp. 2-[*N*-Ethyl-*o*-aminobenzoic acid]-1,4-toluquinone-5, and the corresponding *m*- and *p*-derivatives were prepd. by boiling their constituents in 95% alc., dark violet cryst. powders, and dark red metallic crystals, resp.

D. BREESSE JONES

Succinyldiacetic acid ester. RICHARD WILLSTÄTTER AND ADOLF PFANNENSTIEL. Bayer. Akad. Wiss. *Ann.* **422**, 1-15(1920).—Succinyldiacetic acid is of interest because its C skeleton is suitable as a starting point for the synthesis of cocaine. $\text{CO}(\text{CH}_2\text{CO}_2\text{H})_2$ was prepd. according to Jerdan (*J. Chem. Soc.* **75**, 808). It is catalytically decompd. by PhNH_2 . The ester is best prepd. by adding the acid to a satd. alc. HCl soln. Shaken 1 hr. with twice its wt. of Ac_2O , *acetonedicarboxylic anhydride* is formed, glistening prisms, *m.* 138-40° (decompn.). Concd. HCl at once gives the acid. There also results a *mixed acetic anhydride*, H_3BO_3 -like scales, *m.* 102°. The ester dissolves in NaOH with a deep yellow color, but is quickly decolorized because of a change in constitution of the salt. *Potassium salts* of the *dimethyl* and *diethyl* esters were analyzed. *Dipotassium salt* of *monoethyl acetonedicarboxylate*, rhombic leaflets. FeCl₃ gives a red color with the neutral soln. This salt, after neutralizing the enol-K with acid (best oxalic) is subjected to electrolysis (3-4 amp., 12-14 v. at -5° to 5°) and yields a about 12% *diethyl succinyldiacetate*, $\text{C}_{12}\text{H}_{18}\text{O}_6$, long prisms, *m.* 46-7°. FeCl₃ gives a red color with FeCl₃. The colorless 10% soln. in NaOH deposits small crystals of a *sodium salt*, $\text{C}_{12}\text{H}_{15}\text{O}_6\text{Na}$, thus containing 1 mol. H₂O less than the ester (inner condensation). The *free enol*, $\text{C}_{12}\text{H}_{14}\text{O}_6$, glistening prisms from petr. ether, *m.* 59.5-60°. This gives a blue color with FeCl₃. *Succinyldiacetic acid*, $\text{C}_8\text{H}_{10}\text{O}_6$, by sapon. the ester with concd. HCl, short prisms, *m.* 117°. CO₂ is evolved on melting, giving *acetonylacetone*? PhNH_2 also accelerates this decompn. With MeNH_2 , the ester reacts to give *diethyl N-methylpyrrole-2,5-diacetate*, long prisms, *m.* 163-4°.

C. J. WEST

A complete synthesis of *di*-ecgonine and of tropinone. RICHARD WILLSTÄTTER AND MAX BOMMER. *Ann.* **422**, 15-35(1920).—Succinyldiacetic esters react readily with NH₃ and amines to form pyrrole derivs. Thus AcONH_2 gives *diethyl pyrrole-2,5-diacetate*, $\text{C}_{12}\text{H}_{17}\text{O}_4\text{N}$, prisms, *m.* 74-5°. *N-Methylpyrrole-2,5-diacetic acid*, $\text{C}_8\text{H}_{10}\text{O}_4\text{N}$, obtained by sapon. the ester (see preceding abstr.) with 10% MeOH-KOH, rhombic tables, *m.* 150° (decompn.). *Methyl ester*, $\text{C}_{11}\text{H}_{15}\text{O}_4\text{N}$, long, thin prisms, *m.* 170-1°. Both esters are reduced by H according to the method of Willstätter and Jaquet (*C. A.* **13**, 577). *Diethyl N-methylpyrrolidine-2,5-diacetate*, *b.* 162.5°; *dimethyl ester*, *b.* 155.5°. The Et ester requires 60-70 parts, the Me ester 6-7 parts cold H₂O for soln. Exhaustive methylation gives *diethyl N-methylpyrrolidine-2,5-diacetate methiodide*, tables, *m.* 78°. Upon warming with concd. K₂CO₃ at 60°, a compd. is obtained which again adds MeI. Upon heating with NaOH, MeN is split off, and a *hexadiene-dicarboxylic acid* ($\text{CO}_2\text{HCH}_2\text{CH}=\text{CH}-$)₂, crysts. in fine needles, *m.* 260°. The inner condensation of these reduced esters to tropane derivs. may be carried out with EtONa, NaNH₂ or best, powdered Na metal. The condensation product of the *N*-Me ester, by heating 10 g. ester, 10 cc. cymene and 2 g. Na at 160-72° for 10 min., yields tropinone upon heating with dil. H₂SO₄. This was purified through the picrate and proved to be identical with the natural base. The existence of the β -ketonic acid

ester as an intermediate step in the reaction is shown by its reduction to *dl*- ψ -ecgonine Et ester and transformation into the Me ester, which is known, and also by its transformation into *d*- ψ -cocaine. The various ecgonine esters react more or less easily with NaOH, splitting off Me₃N. The ψ -compd. is about half decompd. after 2 hrs. heating with 25% NaOH. C. J. WEST

Preparation of formaldehyde from ethylene. RICHARD WILLSTÄTTER AND MAX BOMMER. *Ann.* 422, 36-46 (1920).—Pure C₂H₄, mixed with O and N, so that there are about 60% C₂H₄ and 6% O, when heated to 600°, gave 16% HCHO (calcd. on the actual C₂H₄ used in the expt.). At 567° the yield was 32% and at 547°, 38%, though the actual yields in g. were smaller because less C₂H₄ entered into reaction. With 40% C₂H₄ and 4% O, the yield of HCHO was 51% (temp., 800°), while with 20% C₂H₄ and 8% O, at 585°, the yield was 103%, which is about half the theory. W. and B. believe it will be very difficult to utilize the C₂H₄ to any better advantage. C. J. WEST

Constitution of methylloxaluric acid. ROBERT BEHRND AND GUSTAV HARTSL. *Techn. Hochschule, Hannover. Ann.* 422, 74-109 (1921).—The prepn. of methylloxaluric acid (A) from 1,4- or 3,4-dimethyluracil does not enable a conclusion to be drawn between the two possible constitutions, MeNHCONHCOCOC₂H₅ and H₂NCONMeCOCOC₂H₅, for the intermediate product, methylparabanic acid, may give rise to either. Attempts to synthesize A failed. Decompn. expts. with HNO₃ or HBrO likewise gave no insight into the matter. Therefore, attempts were made to obtain acetylation products, which might be decompd. These expts. were not altogether satisfactory, but they seem to indicate the sym. formula. Oxaluric acid is best obtained by dissolving 12.1 g. dibromohydroxymethyluracil and 4.48 g. KOH in H₂O by boiling 30 min., adding 5.38 g. K₂CO₃ and then 4.42 g. KMnO₄ (4%) and oxidizing in the cold. Yield, 83%. The ester can be obtained pure only by treating the Ag salt with EtI in C₆H₆ (alc., Et₂O or AcOEt should not be used); it m. 183-4°. Dimethyluracil may be prepd. by using Me₂SO₄. A is prepd. from 4.7 g. dibromohydroxy-1,4-dimethyluracil by suspending it in H₂O containing 1.7 g. KOH and 2.02 g. K₂CO₃ and oxidizing at 20-30° with 5% KMnO₄ (1.58 g.). The yield is about 41%. The *ethyl ester*, C₈H₁₀O₄N₂, prepd. by shaking the Ag salt, flat needles, with EtI in C₆H₆, prisms, m. 144-6°. The ester is rather stable towards NH₃. Ac₂O and oxaluric acid yield *acetoxaluric acid*, C₈H₈O₄N₂·H₂O, long spears or prisms, m. 140°, and *acetoxaluric acid urea*, C₈H₈O₄N₂·CH₄ON₂, small needles, m. 189° (decompn.). Neutralized with K₂CO₃, it forms C₈H₈O₄N₂·K₂H₂O. The action of Ac₂O upon methylloxaluric acid gave, at 100°, principally methylparabanic acid, which at higher temps. is acetylated to *methylacetylparabanic acid*, C₈H₈O₄N₂, leaflets, m. 182-4°. A small amt. of a substance, perhaps acetylmethylloxaluric acid, m. 175°, is also formed. The action of Ac₂O upon oxaluric ester gave acetoxaluric acid and oxamide, besides a small amt. of oxamethane. Oxamethane is best acetylated by heating with AcCl at 130-40°, giving *acetoxamethane*, m. 54-5°. This gradually decompn. on standing. Warmed in MeNH₂ soln., dimethylloxamide results. PhNH₂ gives oxanilide, and, principally, oxanilic acid ester, m. 63-5°. Parabanic acid, warmed with Ac₂O-AcOH, gave acetoxaluric acid, and its ester. Methylloxaluric ester and Ac₂O gave a considerable amt. of methylacetylparabanic acid, less methylparabanic acid and a sirup, easily sol. in Et₂O, which gave, with NH₃, oxamide, and with MeNH₂, a mixt. of mono- and dimethylloxamide. AcCl gave, in addition to the above, a small amt. of acetoxamethane. Methylparabanic acid is not as readily acetylated by AcCl as by Ac₂O. The fact that the mixt. of the mono- and dimethylloxamide is formed above indicates that, besides acetoxamethane, oxamethane must be present and this can result only if the compd. has the sym. formula.

C. J. WEST

Synthesis of γ -coccinic acid and attempts to synthesize cochenillic acid. C. A. SCHRUESSNER AND H. VOSWINCKEL. Tech. Hochschule, Berlin. *Ann.* 422, 111-33 (1921).—Meldrum (C. A. 6, 627) by the use of Fritsch's $\text{CCl}_3\text{CHO} \cdot \text{H}_2\text{O}$ reaction (*Ann.* 296, 351) was able to synthesize the ester of α -coccinic acid (A), but was not able to split off the Me group and obtain the free acid. S. and V., starting with the free *m*-cresotic acid, instead of the Me ester of the *sym*-acid, have been able to prep. the free acid. 10 g. *m*-cresotic acid and 11 g. $\text{CCl}_3\text{CHO} \cdot \text{H}_2\text{O}$ are rubbed together and then stirred into 50 cc. concd. H_2SO_4 . After 2-3 days the clear soln. becomes turbid and the reaction is ended. Poured into ice-water, 5-methyl-7-hydroxy-3-trichloromethyl-phthalide, (I) $\text{C}_{10}\text{H}_7\text{O}_4\text{Cl}_3 \cdot 0.5\text{H}_2\text{O}$, seps., rose-colored, loses its H_2O at 105° , m. above 300° . Upon concg. the mother liquor of I, 5-methyl-3-hydroxy-2-carboxyphenyltrichloroethanol (II), $\text{C}_{10}\text{H}_7\text{O}_4\text{Cl}_3 \cdot \text{H}_2\text{O}$, seps., long needles, m. 208° . It is obtained also by heating I with H_2O for 1 hr. The alc. soln. gives a deep violet color with FeCl_3 . The yields are: I 12.8 g. II 4 g.; 10 g. I, warmed 5 hrs. with 200 cc. 10% NaOH at 30° , and then allowed to stand 24 hrs. gave upon acidification with HCl, filtration, concn. to dryness, extrn. with Et_2O , and crystn. from hot H_2O , 5-methyl-3-hydroxy-2-carboxy-mandelic acid (III), $\text{C}_{10}\text{H}_9\text{O}_6$, yellowish needles, m. 204° (decompn.). The aq. soln. gives a red color with FeCl_3 . III is obtained also by the action of 400 cc. 5% NaOH, at 50° on 10 g. II. When 5 g. III are dissolved in 100 cc. 5% NaOH and gradually treated with 160 cc. 3% KMnO_4 for 5 hrs. at room temp. and then at 50° , 4 g. A are obtained, which sinter 215° , m. $226-8^\circ$. The barium salt crystals, in fine, white needles with 2 mols. H_2O . The acid A may be prepd. without the intermediate isolation of III, by oxidizing the alk. soln. from I or II with KMnO_4 . Anhydride of A, by heating the acid in an air bath at 210° for 0.5 hr., short, yellow needles from dil. AcOH, m. 209° . Heating with H_2O gives A. Warmed to 200° with resorcinol, it gives a red melt, which gives a yellow soln. with green fluorescence in alc. with NaOH. Acetyl- γ -coccinic acid, $\text{C}_{11}\text{H}_{11}\text{O}_6$, from 2 g. A, 20 cc. Ac_2O and 0.5 g. AcONa , short yellowish prisms from dil. alc., m. 196° . Anhydride, long leaflets, formed by heating 1 g. of the acid with 15 cc. POCl_3 and 10 cc. AcCl 10 min., m. 200° . Ethyl ester of A, $\text{C}_{11}\text{H}_{13}\text{O}_4 \cdot 0.5\text{H}_2\text{O}$, by passing HCl gas into A in alc., long, fine needles, m. 224° (decompn.). FeCl_3 gives an intense violet color. Methyl ester, $\text{C}_{10}\text{H}_{11}\text{O}_5$, m. 202° (Meldrum, 200°). By warming 10 g. I with 200 cc. 15% NaOH 3 hrs. at 80° or until the mixt. no longer has the odor of CHCl_3 , 5-methyl-3,7-dihydroxyphthalide, $\text{C}_9\text{H}_7\text{O}_4$, is formed, yellow leaflets, m. 276° . Sodium salt, yellow needles. FeCl_3 gives a dark blue soln. 5-Methyl-7-hydroxyphthalide (IV), $\text{C}_9\text{H}_7\text{O}_3 \cdot \text{H}_2\text{O}$, is formed when 10 g. I are boiled with 220 cc. concd. Na_2CO_3 for 2 hrs., small, yellowish leaflets, m. 266° . The alc. soln. gives a blue color with FeCl_3 . KMnO_4 oxidizes it to A. IV is also formed by heating II in an air bath at 200° for 0.5 hr. $\text{CCl}_3\text{CHO} \cdot \text{H}_2\text{O}$ does not react with I, while with II, a part is obtained unchanged and a part is changed into I. By treating $\text{CCl}_3\text{CHO} \cdot \text{H}_2\text{O}$ with A, 8% of a Cl-containing product was obtained.

C. J. WEST

Effects of ring closure on spectrochemical properties. II. Unsaturated heterocyclic compounds. K. v. AUWERS. Univ. Marburg. *Ann.* 422, 133-59 (1921); cf. C. A. 13, 432.—In the 1st paper it was shown that the formation of a satd. ring in general had no effect upon optical properties. A change of an unsatd. open chain to an isocyclic ring with the same number of double bonds caused a decrease in the sp. refraction and dispersion. With simple unsatd. cyclic and acyclic compds. the differences are small; with compds. with several unsatd. linkings, the effect is very noticeable. Alkyl groups and other substituents oppose the effect of the ring closure. The depressing action of the ring closure occurs only if, in the resulting closed system, some kind of neutralizing of the valences occurs. In this connection the furans stand at the top, the cou-

vessel used. Above about 69%, the % of C_3H_4 in the gas has little effect upon the degree of absorption by 99.3% acid. The first figure is the purity of the C_3H_4 , the second, the % increase in wt. in each case: 92.7, 3.66; 86.4, 3.87; 84, 3.58; 78.9, 3.62; 72.7, 3.58; 69.6, 3.52; 64.6, 3.41; 59.8, 3.14; 57.3, 2.72; 50.7, 2.62; 46.4, 2.30; 41.4, 2.21; 37.3, 1.91; 29.6, 1.44; 25.2, 1.32; 17.9, 1.06; 8.0, 0.48. The absorption was studied, at 50° for 93.1%, 97.6% and 99.3% acid, at 70° for 93.1, 95.8, 98.1, 98.8 and 100.1% acids, at 100° for 93.1, 98.1 and 100.1% acids and at 125° for 93.1 and 100.1% acids, and by oleum at 70°. Figures and curves are given in the original. The products in each case were analyzed, but at 100° and 125° decompn. was so marked that the figures are of little value.

Acid strength.	Increase in wt.	$EtHSO_4$.	Et_2SO_4 .	H_2SO_4 .	H_2O .	Temp.
93.1	16.56	60.1	0	33.9	6.	50
97.6	29.23	73.9	15.8	8.4	1.9	50
99.3	32.01	72.7	22.2	4.6	0.5	50
93.1	20.83	69.5	2.2	22.5	5.8	70
95.8	27.98	79.1	9.4	8.2	3.3	70
98.1	34.25	74.8	20.3	3.5	1.4	70
98.8	36.23	68.1	29.3	1.7	0.9	70
100.1	38.62	70.0	30.0	70

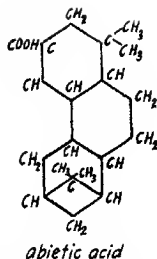
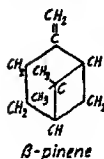
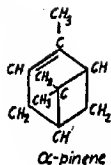
There are 3 successive stages in the absorption: Soln. of C_3H_4 in the liquid, its reaction with H_2SO_4 to give $EtHSO_4$ and its reaction with $EtHSO_4$ to give Et_2SO_4 . The 2nd and 3rd reactions may proceed together and probably do. They proceed at rates which are proportional to the products of the concn. of the C_3H_4 and the concn. of the H_2SO_4 and $EtHSO_4$, resp. $EtHSO_4$ has a distinctly autocatalytic effect. This can be explained by the greater soly. of C_3H_4 in the liquid phase as $EtHSO_4$ accumulates in the system. Et_2SO_4 begins to appear after about a 20% absorption (by 98% acid). 7.9% is present after 25.14% increase in wt., 14.5 after 29.37%, and 21.1 after 32.42% increase. The influence of H_2O in the H_2SO_4 is found to be small apart from its retarding action upon the absorption in general. The amt. of Et_2SO_4 present at any given degree of absorption is practically independent of the strength of the acid used. The absorption of C_3H_4 is more complicated and has not been reported in detail.

C. J. WEST

The location of the double bond in ricinoleic acid. K. STOSIUS and K. WIESLER. *Biochem. Z.* 111, 1-7 (1920).—The oxidation of ricinoleic acid in alk. soln. with $KMnO_4$ yields both azelaic and suberic acids. The cause of the formation of suberic acid together with the azelaic acid may be the presence in ricinoleic acid of the 2 isomers $Me(CH_2)_7CH(OH)CH_2CH:CH(CH_2)_7CO_2H \rightleftharpoons Me(CH_2)_7CH(OH)(CH_2)_7CH:CH(CH_2)_7CO_2H$, in equil., the formation of suberic acid by oxidation of azelaic acid, or that equil. in the possible isomers is obtained in alk. soln. I shown exply. that the second proposition is invalid. The conception of the existence of isomeric forms in equil. is considered as of doubtful value from the fact that oxidation with either HNO_3 or alk. $KMnO_4$ yields both suberic and azelaic acids. The latter proposition is developed by analogy from Fittig's studies (*Ber.* 24, 82(1891); 26, 40 (1893); 27, 2876(1894)).

F. S. HAMMETT

The constitution of abietic acids in rosin. A. GRÜN. *Aussig. Z. deutsch. Oel-Fett Ind.* 41, 49-52(1921).—An attempt to formulate the structure of abietic acids from rosin to show their relationship to α - and β -pinene and to explain their behavior toward halogens and their changes during destructive distn. References are given to Bucher's, Tschirch's and Frankforter's work. The following formulas among others are suggested as a working hypothesis rather than final conclusion:

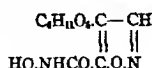


The abietic acid here shown is formed from one atom each of α - and β -pinene by giving the two Me groups in α -pinene a *m*-position and turning the formula by 60° toward the left and then writing the β -pinene underneath. This structure for abietic acid shows only an isomeric relation toward retene, a by-product of decompn. of abietic acid by dry distn., but G. considers this objection as secondary, not as fundamental.

P. ESCHER

Hiptagin, a new glucoside from *Hiptage medabiota*, Gaertn. K. GORTER. *Bull. Jard. bot. Buitensorg* (3) 2, 187-202(1920).—This glucoside is extd. in a yield of 8% from the root bark by acetone or EtOAc. The bark of the stem contains much less. *Hiptagin*, $C_{10}H_{16}O_4N_2 \cdot \frac{1}{2}H_2O$, forms silky needles, m. 110° , $[\alpha]_D^{20}$ 3.5° in 5% acetone soln. The most characteristic chem. property is the formation by dil. alkali hydroxide, even in the cold, of NH_3 and HCN. Dil. acids act quite differently, forming dextrose, and, at the same time, breaking down the genin in various ways; 5% aq. H_2SO_4 at 100° forms tartaric acid. Concd. HCl, mixed with 4 vols. of acetone, forms in five days at the ordinary temp. strong, monobasic *hiptagenic acid*, $C_8H_{10}O_4N$, needles, m. 68° , $k = 1.20 \times 10^{-4}$, giving cryst. *silver, lead, and zinc salts*. The hypothetical hiptagenin is decompd. according to the equation $C_8H_{10}O_4N_2 + 2H_2O = C_8H_{10}O_4N + CO_2 + NH_3$. Hiptagenic acid is formed also by destructive distn. of the glucoside, and is regarded as having the constitution $HONHCOC(OH):CHOH$. By heating hiptagenic acid with HCl on the water bath, it is hydrolyzed to diglycolic and formic acids and to $NH_3 \cdot OH \cdot HCl$, $2C_8H_{10}O_4N + 3H_2O = C_8H_{10}O_4 + 2HCO_2H + 2NH_3 \cdot OH$. NaOEt at the ordinary temp. decomp. hiptagin, with the formation of $NaNO_3$, but hiptagenic acid is only slowly hydrolyzed by boiling alc. NaOEt soln., probably with the formation of formhydroxamic acid (red color with $FeCl_3$) and of glyoxal; $HOCH:C(OH)CONHOH = HOCH:NOH + (CHO)_2$. The action of aq. alkalis on hiptagenic acid is very complex. The best results were obtained by heating with $Ba(OH)_2$ at 50° , which formed $Ba(NO_3)_2$, Ba formhydroxamate, and (in 72% yield) a salt, $C_8H_9O_4NBa$. The latter is regarded as derived from a carbamic acid, $HOCH:C(OH)NHCO_2H$, isomeric with hiptagenic acid. On heating with H_3PO_4 , the Ba salt gives half a mol. proportion of CO_2 , HCN and $(CO_2H)_2$, NH_3 , CH_2O , and glyoxal. The isomerization of hiptagenic to the carbamic acid is compared to the Beckmann transformation of oximes. The carbamic acid may be decompd. on the one hand to NH_3 and glyoxal, and on the other to CH_2O , water, and $NCCO_2H$. The last-named may yield HCN and CO_2 , or $(CO_2H)_2$ and NH_3 . Glyoxal and CH_2O were obtained as *p*-nitrophenylhydrazones. The action of $Ba(OH)_2$ on hiptagin takes place according to the equation $C_{10}H_{16}O_4N_2 + 3H_2O = C_8H_{10}O_4 + C_2H_5O_2N + CO_2 + NH_3$. The Ba salt of the carbamic acid here has the compn. $(C_8H_9O_4N)_2Ba$, and appears to be derived from the tautomeric form, $CHOCH(OH)NHCO_2H$, without the two acid

hydroxymethylene groups formulated above for the salt from hiptagenic acid. G. proposes for hiptagin the annexed formula of an isoxazole deriv. He considers that

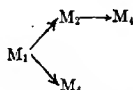


it is formed in the plant by reduction of nitrates to NH_2OH , and condensation of this base with aldehydes and ketones. J. C. S.

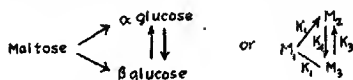
Chemistry of diastase. I. Constitution of maltose from the standpoint of the chemical dynamics of its hydrolysis. EICHI YAMAZAKI AND NOBUO YAMADA. *J. Tokyo Chem. Soc.* 41, 621-90(1920).—Since maltose is not hydrolyzed by emulsin, it is an α -glucoside, but what kind of glucose the reducing portion of the maltose is, is not known. Y. and Y. studied this question from the chem. dynamics of its hydrolysis. The method is as follows: Maltose is hydrolyzed by maltase (Takadiastase, Sankyo), at pH 4.7 under various conditions, and its hydrolysis const. are detd. The reducing part of the maltose may be either (I) α - and β -glucose, (II) α -glucose, or (III) β -glucose. In I reaction should go from maltose $\rightarrow \gamma'$ -glucose + α -glucose \rightarrow 2 γ -glucose, *i. e.*, $M_1 \xrightarrow{K_1} M_2 + M_4 \xrightarrow{K_2} 2M_4$. In II maltose \rightarrow 2 α -glucose \rightarrow 2 γ -glucose, *i. e.*, $M_1 \xrightarrow{K_1} 2M_2 \xrightarrow{K_2} 2M_4$. In III maltose \rightarrow α -glucose + β -glucose \rightarrow 2 γ -glucose, *i. e.*



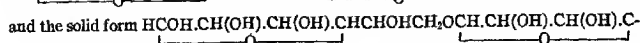
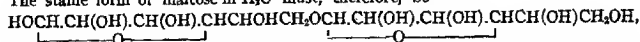
or it can be considered as



The concns. of these products, during hydrolysis at any time t , *i. e.*, C_{M_1} , C_{M_2} , C_{M_3} , and C_{M_4} are calcd. and compared with the exptl. data. The conclusion is that maltoses contain β -glucose (reducing part) and α -glucose (non-reducing part). Successive hydrolysis of maltose is, then, expressed as



The stable form of maltose in H_2O must, therefore, be



$\text{HCH}(\text{OH})\text{CH}_2\text{OH}$. The actual concns. of M_1 , M_2 , M_3 at t can be calcd. from the formulas: $C_{M_1} = ae^{-k_1t}$; $C_{M_2} = [a_2 + \frac{1}{k_3 + k_4 - k_1} \{ (a(k_1 - k_4)e^{-k_1t} - k_1a_2e^{-(k_3 + k_4)t}) \}] + a_2[1 - \frac{1}{k_3 + k_4 - k_1} \{ (k_3 + k_4)e^{-k_1t} - k_1e^{-(k_3 + k_4)t} \}]$; $C_{M_4} = a_1 + \frac{1}{k_3 + k_4 - k_1} \{ (a(k_1 + k_4)e^{-k_1t} - k_1a_1e^{-(k_3 + k_4)t}) \} + a_1[1 - \frac{1}{k_3 + k_4 - k_1} \{ (k_3 + k_4)e^{-k_1t} - k_1e^{-(k_3 + k_4)t} \}]$ where $K_1 + K_4 = K_1$. The similar analysis applied to the data for sucrose obtained

by Hudson and Nelson convinced Y. and V. that the structural formula suggested by Haworth for this sugar is more probably correct than that of Fischer. S. T.

Report on the essential oil of *Artemisia annua* L. II. Constitution of artemisia ketone. YASUHIKE ASAHINA AND SEIJI TAKAGI. *J. Pharm. Soc. Japan* 1920, No. 464, 837-64.—A. and Yoshitomi discovered (cf. *C. A.* 11, 3094), that *Artemisia annua* L. contains a new ketone, $C_{10}H_{16}O$, which does not correspond to any known terpene ketone, but which has 2 double bonds belonging to the aliphatic group. A structural formula for this new compd. has now been worked out in the following manner. First, an attempt to obtain an oxime from tetrahydroartemisia ketone (A) and an acid amide by the Beckmann rearrangement and then to decomp. the product, was not successful. Second, since such ketones ordinarily have the general formula R_2CCOR' , and their CO can easily be oxidized, A. and T. treated it with Beckmann's reagent containing $K_2Cr_2O_7 + H_2SO_4$. After a prolonged reaction, they isolated 7, a compd. giving a typical CH_3 reaction (acetone?); 2, $AcOH$; 3, a caproic acid, $C_6H_{11}O_2$, m. 180° , and its anilide, m. $91-2^\circ$. Since of all isomers of caproic acid, Me_3CEtCO_2H (B) (m. 187°) corresponds most nearly in m. p. to their caproic acid, they prepd. B and its anilide, which m. $91-2^\circ$. Therefore, the formula of A must be $Me_3CEtCOC_2H_5$. Next by boiling A with concd. HNO_3 , they obtained nitrotetrahydroartemisia ketone (its semicarbazone m. 247°) and B, the yield of B being much greater than that produced by Beckmann's reagent. From the mother liquid after sepg. the semicarbazone, they found another compd., having the compn. $C_{10}H_{16}O:NH_2CONHNH_2.H_2O$ (m. about 70° , and anhydrous, $103-4^\circ$) which is basic, sol. in acids, hut pptd. by alkalis. By adding Na_2 to its soln. in weak HCl , they isolated the azide, which is insol. in H_2O , and which, gives off NH_3 and an oily substance when boiled with KOH . This oil, $C_{10}H_{16}O$, is very similar to artemisia ketone in respect to d., $[\alpha]$, and h. p., hut, unlike it, does not give a semicarbazone, but instead, forms a compd. with semicarbazide and then an azide, finally going back to the ketone. When hydrogenated, it goes over to A. This new oil is *isoartemisia ketone*. Since mineral acids often change an unsatd. ketone into more stable α - and β -forms, the iso-form might have been formed during the process of prepn. In fact A. and T. did obtain a trace of azide by treating normal artemisia ketone with semicarbazide and by adding Na_2SO_4 to the mother liquid after sepn. of the semicarbazone. Ordinarily, therefore, about 10% of this ketone is present with the normal ketone, the amt. depending, however, on the amt. of the different reagents used. When artemisia ketone is boiled in 5% alc. H_2SO_4 , 100% goes over to the iso-ketone. A. and T. show, however, that in the essential oil of *Artemisia*, both forms of ketone are naturally present. When the iso-ketone is treated with NH_2OH it gives two compds., $C_{10}H_{16}(NOH)(NH_2OH)$ and $C_{10}H_{16}O(NH_2OH)$, which can be sepd. out by petroleum ether. When hydroxylaminoisoartemisia ketone is dissolved in $CHCl_3$ and oxidized with HgO , it gives a true nitroso compd. $C_{10}H_{17}ONO$, which, therefore, must have the formula $Me_3C(CH:CH_2)CH_2CMe_2NO$. Consequently, the formula is given for isoartemisia ketone as $Me_3C(CH:CH_2)COCH:CM_2$, for the normal ketone as $Me_3C(CH:CH_2)COCH_2CMe:CH_2$. Various chem. and physical const. for all these compds. are given. S. T.

The constituents of *Pelvetia wrightii*, Yendo. KINSUKE KONDŌ. *J. Sac. Agr. Forestry, Sapporo.* 12, 353-66(1920).—By hydrolyzing 3 kg. *Pelvetia wrightii*, Yendo, with 4% H_2SO_4 for 1-2 hrs. on the water bath, 140 g. of a sirupy substance were obtained from which about 60 g. of fucose phenylhydrazone were isolated. By treating it with BzH and alc., 19 g. fucose were obtained, which gave 28.6% methylfurfure. The residual soln., from which the hydrazone had been prepd., gave a sirup by concn., from which arabinose phenylosazone and crystd. arabinose were isolated by Fischer's method. The presence of pentosan (6.40%) and methylpentosan (2.04%) in the air-dried sample was proved, but that of mannitol and galactan was not. K. K.

The formation of anthracene from benzene and ethylene. J. E. ZANETTI AND M. KANDELL. *J. Ind. Eng. Chem.* 13, 208-11(1921).—A mixt. of C_6H_6 and C_2H_4 obtained by bubbling C_6H_6 into C_2H_4 heated to about 80° was passed through a quartz tube heated electrically to temps. varying from 800° to 1000° and the gaseous products formed were led through a Cu coil condenser cooled by ice. The fog that collected in the receiver was pptd. electrically by the Cottrell method. The C_2H_4 was bubbled through the C_6H_6 at the rate of 2 cu. ft. per hr. and the heating of the C_6H_6 so regulated that in the gaseous mixt. the ratio by vol. of C_6H_6 to C_2H_4 was 2:1. The tar formed was washed from the condenser with C_2H_6 , added to the filtrate and the whole distd. up to 300° . After the removal of the C_6H_6 , Ph_2 ($250-75^\circ$) distd. and the tar remaining in the flask was extd. with AcOH. The anthracene present in the tar ext. was detd. by weighing the anthraquinone formed on oxidation with CrO_3 . A temp. of 925° gave the max. yields of both tar (15.15% of the C_6H_6 decompd.) and anthracene (0.675% of the C_6H_6 decompd.). At this temp. also the sum of the yields of Ph_2 and carbon was a minimum. Above this temp. carbonization occurred rapidly and was complete at 1000° . Numerous other compds. are formed in the reaction. The reaction is strongly endothermic but only small yields of anthracene can be obtained, since it will not form at low temps. and decomp. above 900° . Correction. *Ibid* 358. G. W. STRATTON

Derivatives of γ -aminovaleraldehyde. BURCKHARDT HELFERICH AND WALTER DOMMER. Univ. Berlin. *Ber.* 53B, 2004-17(1920).—The object of the present work was to det. whether γ - NH_2 aldehydes, like the simple γ -HO aldehydes (*C. A.* 14, 1833), exist not only in the open-chain hut, by migration of a H atom, pass over largely into a cyclic form. Previous attempts to prep. γ - NH_2 aldehydes had led only to the formation of compds. with 1 mol. less of H_2O , i. e., pyrroline or its derivs. (cf. Gabriel, *C. A.* 3, 2137, and earlier workers). Ozone cleavage of $MeCH(NH_2)CH_2CH_2CH:CM_2$ (A) and reduction of the ozonide gave only aq. solns. of γ -aminovaleraldehyde, from which no analyzable product could be isolated. No better success was had with the *N*-dimethyl deriv. of A hut with its *N*-acyl derivs. the desired results were obtained. ζ -Chloro- β -methyl- β -heptene (B), $MeCHClCH_2CH_2CH:CM_2$, obtained in 18-g. yield from 27 g. dry C_4H_7N and 40 g. $MeCH(OH)CH_2CH_2CH:CM_2$ in ice slowly treated with 40 g. $SOCl_2$, heated 0.5 hr. at 180° , dild. with H_2O , extd. with Et_2O , washed with 10% Na_2CO_3 and dried with Na_2SO_4 , $b_D^{18.0}$ 60-1°, $n_D^{18.0}$ 1.4458, $d_4^{18.0}$ 0.8931; 7 g. in 10 cc. cold AcOH subjected to O_3 cleavage until there is no further reaction for the double bond with Br in AcOH, dild. with 60 cc. Et_2O , shaken with Zn dust (10 g.) to reduce the peroxides until KI-starch paper is no longer turned blue, filtered, shaken with concd. K_2CO_3 and dried with K_2CO_3 , gives 3.5 g. γ -chlorovaleraldehyde, $b_D^{18.0}$ 70-1°, $n_D^{18.0}$ 1.4476, $d_4^{18.0}$ 1.0724, reduces warm Fehling soln. and NH_4AgNO_3 at room temp., at once reddens fuchsin- SO_2 ; 9 g. allowed to stand 36 hrs. in 63 cc. MeOH with 1-2% HCl, made alk. with solid K_2CO_3 , freed from most of the MeOH *in vacuo*, taken up in H_2O containing a drop of NaOH, extd. with Et_2O and dried with K_2CO_3 , yields 4.5 g. of the dimethylacetal, $b_D^{18.0}$ 76°, $n_D^{18.0}$ 1.4235, $d_4^{18.0}$ 1.0116, does not reduce boiling Fehling soln., converted back into the aldehyde by dil. H_2SO_4 . ζ -Dimethylamino- β -methyl- β -heptene (6 g. from 11 g. B heated 4 hrs. at 180° with 20 g. of 30% alc. $NHMe_3$), $b_D^{18.0}$ 69°, $n_D^{18.0}$ 1.4440, $d_4^{18.0}$ 0.7965. A (Wallach, *Ann.* 309, 26), $b_D^{18.0}$ 65-6°, was obtained in 24-g. yield from 32 g. $MeC(:NOH)CH_2CH_2CH:CM_2$ in 100 cc. boiling alc. quickly treated with Na, 100 cc. more alc. being added as the soln. of the Na slows up until a total of 400 cc. alc. and 43 g. Na has been used. ζ -Formylamino- β -methyl- β -heptene (9 g. from 20 g. A and 15 g. of 75% HCO_2H heated 1 hr. over a free flame under a reflux), $b_D^{18.0}$ 143, $n_D^{18.0}$ 1.4669, $d_4^{18.0}$ 0.92003, evolves a weakly penetrating odor when warmed with H_2O and when heated with 33% KOH a vapor producing violent coughing; 20 g. in 30 cc. AcOH subjected to O_3 cleavage as above yields

2.3 g. of γ -formylaminovaleraldehyde, $\text{HCONHCHMeCH}_2\text{CH}_2\text{CHO}$ (oxo-form) or $\text{HCON.CHMe.CH}_2\text{CH}_2\text{CHOH}$ (cyclo form), b_D^{25} 84°, reacts acid to litmus, reduces

Fehling soln. and $\text{NH}_4\text{-AgNO}_3$ at room temp. *l*-Acetylamino- β -methyl- β -heptene (8 g. from 13 g. A refluxed 1 hr. with 24 g. Ac_2O), b_D^{15} 150-1°, $n_D^{18.0}$ 1.4651, $d_4^{18.0}$ 0.9142, when boiled with 30% KOH evolves a vapor producing violent coughing; 11 g. gives by the O_3 cleavage 4.5 g. of γ -acetylaminovaleraldehyde (C), b_D^{18} 102-3°, $n_D^{18.0}$ 1.4695, $d_4^{18.0}$ 1.054, reduces warm Fehling soln., slowly reddens fuchsin- SO_3 , gradually reduces $\text{NH}_4\text{-AgNO}_3$ at room temp., becomes turbid and evolves a penetrating odor when warmed with NaOH, reacts acid to litmus. *l*-Propionylamino- β -methyl- β -heptene (D) (12 g. from 30 g. A and 10 g. EtCOCl), b_D^{18} 156°, $n_D^{18.0}$ 1.4648, $d_4^{18.0}$ 0.9084, evolves no amine odor when warmed with H_2O but with 33% KOH gives a vapor producing coughing. The product of O_3 cleavage loses H_2O on distn., yielding *l*-propionyl-5-methyl- Δ^4 -pyrroline, $\text{EtCON.CHMe.CH}_2\text{CH:CH}$, b_D^{18} 98-9°, $n_D^{18.0}$ 1.4852, $d_4^{18.0}$ 1.0013,

reduces Fehling soln., very gradually reddens fuchsin- SO_3 , evolves a penetrating odor when heated with 33% KOH, reacts acid to litmus. *l*-Benzoylamino- β -methyl- β -heptene (6 g. from 12 g. A and 6 g. BzCl in ice), needles from 33% alc., m. 87-8°; 5 g. subjected to O_3 cleavage and distd. gives 1.5 g. *l*-benzoylamino-5-methyl- Δ^4 -pyrroline, b_D^{18} 141-2°, $n_D^{18.0}$ 1.5559, $d_4^{18.0}$ 1.0974, reacts acid to litmus in H_2O , feebly reduces Fehling soln. on warming, very slowly reddens fuchsin- SO_3 , evolves a strongly basic odor with boiling alc. NaOH. The acid reaction of the above γ -acylaminovaleraldehydes and their slow reaction with fuchsin- SO_3 and $\text{NH}_4\text{-AgNO}_3$ are indications that they exist, in part at least, in a cyclo-form, but the best proof of this is afforded by their behavior towards HCl in MeOH. Thus 6 g. C allowed to stand 36 hrs. in 42 cc. MeOH with 1-2% HCl gives 3.5 g. of the hemiacetal (*l*-acetyl-2-methyl-5-methoxypyrrolidine), b_D^{18} 112°, $n_D^{18.0}$ 1.4650, $d_4^{18.0}$ 1.0276, has a faintly basic odor, neutral to litmus in H_2O , unchanged by heating with H_2O , deposits oil droplets and evolves a basic odor when heated with NaOH, does not reduce boiling Fehling soln. unless it has been heated 10 min. on the H_2O bath with 5 *N* H_2SO_4 . Similarly, 6 g. of the crude (undistd.) O_3 cleavage product of D with 1% HCl in MeOH yields 3.5 g. of γ -propionylaminovaleraldehyde hemiacetal (*l*-propionyl-2-methyl-5-methoxypyrrolidine), b_D^{18} 122-3°, $n_D^{23.0}$ 1.4599, $d_4^{23.0}$ 1.0029, has a faint amine-like odor, is less sol. in a little H_2O at room temp. than at lower temps., does not reduce boiling Fehling soln. until after it has been heated 10 min. on the H_2O bath with 5 *N* HCl. C has a pronounced narcotic action on frogs and rabbits; in the latter it markedly slows the respiration without affecting the blood pressure.

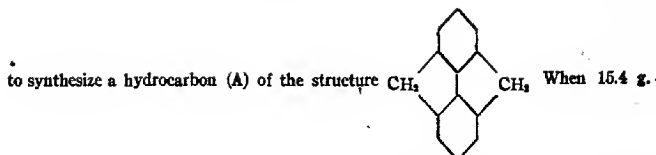
CHAS. A. ROULLER

Sulfoxyl compounds. XI. Derivatives of hydrosulfamine. A. BINZ AND E. HOLZAPFEL. Georg-Speyer-Haus, Frankfurt a.M. *Ber.* 53B, 2017-29 (1920); cf. C. A. 12, 1189.—Of the few isolated processes described in the literature none is simple enough or sufficiently capable of extension to afford a general means of synthesizing derivs. of hydrosulfamine (thiohydroxylamine), NH_2SH . This object, however, can be effected by treating the condensation products of $\text{HOCH}_2\text{OSONa}$ (A) and aromatic amines with org. monosubstitution products of H_2S . A (10 g.) in 10 cc. H_2O with 6 cc. AcSH in 15 cc. of 50% MeOH reacts according to the equation $\text{HOCH}_2\text{OSOH} + \text{AcSH} = \text{AcOH} + \text{HCHO} + 2\text{S} + \text{H}_2\text{O}$. Diformaldehydesulfoxylic acid in $\text{EtOH-Et}_2\text{O}$ also reacts with alc. H_2S with disappearance of the reducing action on indigo carmine and gradual deposition of yellow crystals which are apparently S. It might be expected, therefore, that if the A were previously condensed with an amine, RNH_2 , it would decomp. according to the equations $\text{RNHCH}_2\text{OSOH} + \text{AcSH} = \text{RNH}_2 + \text{AcOH} + \text{HCHO} + 2\text{S}$ or $\text{RNHCH}_2\text{OSOH} + \text{AcSH} = \text{RNHAc} + \text{H}_2\text{O} + \text{HCHO} +$

25. However, these reactions occur only to a minor extent, if at all, the chief reaction being $\text{RNHCH}_2\text{OSO}_3\text{H} + \text{AcSH} = \text{RNHSAc} + \text{HCHO} + \text{S} + \text{H}_2\text{O}$. This can be explained on the assumption of a tendency to the formation of a labile HSOH and its derivs. RSOH (cf. Heinze, C. A. 14, 26, and earlier workers). A then, with AcSH, would give, besides HCHO, AcSOH and HSOH, which decomp. into S + AcOH and S + H₂O, resp., while the RNHSAc formed in the case of RNHCH₂OSO₃H does not decomp. Mercaptans and PhSH react like AcSH on aryliminomethylenesulfoxylates; the reaction seems to be quite general, although it does not always lead to clear-cut results. All these derivs. of NH₂SH are yellow, stable when protected from the air, decomp. somewhat in the air in the course of several days, becoming red, small amts. of S and the mercaptan component splitting off; cold dil. acids and alkalis have no action on them. Sodium anthraniliminomethylenesulfoxylate (B), $\text{o-HO}_2\text{CC}_6\text{H}_4\text{NHCH}_2\text{OSONa} \cdot 2\text{H}_2\text{O}$ (25 g. from 30 g. anthranilic acid (C) added in small portions to 40 g. A in 40 cc. H₂O at 70–80° and filtered through a hot funnel), m. 96°, reduces hot indigo carmine, relatively stable *in vacuo*, slowly oxidizes in the air, becoming yellow. The freshly prepd. B from 30 g. C treated in 150 cc. H₂O with 10 g. AcSH, dild. with an equal vol. of H₂O when the reaction is complete (when indigo carmine is no longer reduced), filtered, washed with much H₂O, dried on clay (yield 20 g.), twice dissolved in 5 parts cold Et₂O and filtered from S and crystd. from AcOEt gives *S-acetyl-o-hydrosulfamino benzoic acid* (*N-sulfacetylanthranilic acid*), $\text{HO}_2\text{CC}_6\text{H}_4\text{NHSAc}$, faintly yellow, m. 133°, sol. in most org. solvents, NaOH and soda, fluoresces in alc. like C but is not sweet, forms with metallic salt ppts. which decomp. on heating. *S-Ethyl-o-hydrosulfaminobenzoic acid* (14 g. from the B from 25 g. C shaken 4 hrs. in 100 cc. H₂O with 6 g. EtSH in sealed vessels filled with N), small crystals from AcOEt, m. 97–9°. *S-Phenyl analog* (9 g. from 20 g. B and 10 g. PhSH in 150 cc. H₂O acidified with HCl), small crystals from AcOEt, m. 111°. Sodium *p*-carboxyphenyliminomethylenesulfoxylate (D), $\text{p-HO}_2\text{CC}_6\text{H}_4\text{NHCH}_2\text{OSONa} \cdot 2\text{H}_2\text{O}$, similar in properties to B, is obtained in 43 g. yield from 30 g. *p*-H₂NC₆H₄CO₂H and 40 g. A in 40 cc. H₂O at 75°. *S-Acetyl-p-hydrosulfaminobenzoic acid* (22 g. from 25 g. D in 50 cc. H₂O and 10 g. AcSH), faintly yellow crystals from AcOEt, m. 159–60°. *S-Ethyl compound*, from the D from 30 g. *p*-H₂NC₆H₄CO₂H in 150 cc. H₂O and 10 g. EtSH in a N atm. shaken 4 hrs. and allowed to stand 24 hrs.), small crystals from AcOEt, m. 121°. *o*-Phenylenediaminomonomethylenesulfoxylic acid, $\text{C}_7\text{H}_{10}\text{O}_2\text{N}_2\text{S} \cdot 2\text{H}_2\text{O}$, is obtained in 7 g. yield as a finely granular, gray-white substance (somewhat oxidized, N 11.74%, S 11.74%, S:I in titration with I 1:3.01) from 18 g. *o*-C₆H₄(NH₂·HCl)₂ in 50 cc. H₂O and 15.4 g. A in 10 cc. H₂O; it reduces cold indigo carmine even after standing 24 hrs. in the air; 11 g. in 50 cc. H₂O treated with 7.6 g. AcSH gives 6 g. C₇H₄(NHAc)₂, m. 185–6°, but no NH₂SH deriv. From 20 g. A in 20 cc. H₂O at 70° treated with 30 g. H₂NC₆H₄AsO₂Na·3H₂O in small portions, dild. with H₂O to 120 cc. and warmed with 250 cc. of 2/3 N magnesia mixt. is obtained 21 g. sodium magnesium arsenilidimethylenesulfoxylate, $\text{NaOSOCH}_2\text{NHC}_6\text{H}_4\text{AsO}_2\text{Mg} \cdot 2\text{H}_2\text{O}$, sol. in dil. acids, reduces hot indigo carmine. The Mg-free Na salt could not be isolated; if the soln. of the condensation product is concd. there is obtained an unfilterable gel. If, however, the brown-yellow soln. resulting from 20 g. A in 20 cc. H₂O and 30 g. of the arsenilate at 70° is dild. to 100 cc. and treated cold with 30 cc. AcSH in small portions there is formed a resinous yellow ppt. which solidifies overnight and in the liquid there remains a whitish suspension (see below). The yellow ppt. dissolves in 40 cc. C₆H₅N with red color and 80 cc. MeOH ppts. 11 g. of a red substance, m. 183° (decompn.), having the compn. of *S-acetylhydrosulfaminophenyl-L-arsine disulfide*, $\text{AcSNHC}_6\text{H}_4\text{AsS}_2$, while the supernatant fluid with the white suspension, when treated with excess of dil. HCl, yields in the course of several hrs. an abundant yellow ppt. which, washed with H₂O, MeOH and Et₂O, digested with CS₂, dried *in vacuo* (20 g.)

and pptd. from C_6H_5N with MeOH, gives bis-[S-acetylhydrosulfaminophenyl]-4,4'-arsine sesquisulfide, $(AcSNHC_6H_4As)_2S_3$, sinters 150° , m. 159° (decompn.). B (20 g.) in 100 cc. H_2O (protected from the air) treated 1 hr. with H_2S gave a white ppt. sol. in Et_2O and remaining, on evapn. of the Et_2O , in amorphous yellowish scales (3 g.), m. 116° , having the compn. of bismethyleneanthranilino trisulfide, $(HO_2CC_6H_4NHCH_2)_2S_3$, sol. in NaOH and soda, the alk. soln. gradually depositing S, reduces indigo carmine; when pptd. from dil. NaOH with AcOH and again taken up in Et_2O and evapd. it softens 40° and m. 70° , without changing in compn. From 25 g. B in 100 cc. H_2O at $40-50^\circ$ treated 2 hrs. with $H_2Se + H_2$, then with H_2 to drive out the excess of H_2Se , dild. with an equal vol. of H_2O , filtered, dried *in vacuo* on clay, digested twice with 100-cc. portions of Et_2O (which leaves a large amt. of a red substance, apparently Se, undissolved), and evapd. *in vacuo* there is obtained 5 g. of yellow scales of the compn. $C_{14}H_{10}O_2N_2S_2Se$, sinters 50° , m. 125° (decompn.), quickly decomp. in air in alk. soln. with deposition of Se. $p\text{-}C_6H_4(NH_2)_2$ (20 g.) in 20 cc. H_2O and 14 cc. HCl (d. 1.19) treated with 28.5 g. A in 20 cc. H_2O gives in a few min. the compd. $H_2NC_6H_4NHCH_2OSO_2H$ in reddish cryst. scales, which is so readily oxidized that it is drained only to the point where it is still just covered with liquid; in this state about 20 g. is stirred up quickly with 200 cc. air-free H_2O , dissolved by the addition of 15 cc. HCl (1.19) and treated 1 hr. with H_2Se , giving 7 g. of a substance having the compn. $C_{14}H_{10}O_2N_2S_2Se \cdot HCl$, m. $183-4^\circ$, insol. in alkalies and org. solvents, completely sol. with blood-red color in $(CH_3NH_2)_2$. XII. Action of oxidizing agents on formaldehydesulfoxylates. A. BENZ AND E. HABERLAND. *Ibid* 2030-4.—As neosalvarsan, the condensation product of salvarsan with $HOCH_2OSO_2Na$ (A), is being used together with $HgCl_2$ (Löwenstein, *Med. Klinik* 16, 233(1920)), it has become necessary to det. what reaction takes place when the two substances are mixed. Preliminary expts. have shown that the process is quite complicated and its explanation requires a knowledge of the simpler reaction between A itself and $HgCl_2$. When 2.71 g. $HgCl_2$ in 100 cc. H_2O is treated with 0.77 g. A, $2H_2O$ in 60 cc. H_2O , there is at once pptd. 1.8 g. of $HgCl$. Again, 0.542 g. $HgCl_2$ in 20 cc. H_2O treated with 0.154 g. A in 10 cc. H_2O gives a white ppt., which is filtered after 18 hrs.; the filtrate does not decolorize indigo carmine (indicating the disappearance of sulfoxyl S) and absorbs no I (showing that the H_2SO_3 present is combined with HCHO); after addition of $NaHCO_3$ it requires 19.8 cc. of 0.1 N I; after boiling with HCl it gives no reaction for H_2SO_3 . $HgCl_2$ (0.677 g.) in 25 cc. H_2O digested 0.5 hr. at 60° in a closed flask with 0.8355 g. A gives a somewhat grayish ppt. of $HgCl$; titration of 10 cc. of the filtrate with I (excess of the sulfoxyl S) and again after addition of $NaHCO_3$ (sulfite S) shows that 0.0878 g. sulfoxyl S has disappeared and 0.0768 g. sulfite S been formed. Finally, 0.308 g. A in 20 cc. H_2O and 0.271 g. $HgCl_2$ in 10 cc. H_2O allowed to stand overnight in a closed vessel give a ppt. of Hg with a little $HgCl$ and titration of 5 cc. of the liquid shows 0.0312 g. sulfoxyl S disappeared and 0.0298 g. sulfite S formed. These expts. indicate that the reaction may be represented by the equations $A + 2HgCl_2 + H_2O = HOCH_2OSO_2H + 2HgCl + NaCl + HCl$ and $A + 2HgCl_2 + H_2O = HOCH_2OSO_2H + 2Hg + NaCl + HCl$. The reaction between A and $Na_2S_2O_4$ is analogous to that between $Na_2S_2O_4$ and $Na_2S_2O_3$ (*Ber.* 38, 3830(1905)), a labile thioformaldehydesulfoxylate probably being formed as intermediate product: $A + Na_2S_2O_4 = HOCH_2OS_2ONa$ (B) + Na_2SO_3 ; $B + 2NaOH = HOCH_2OSO_2Na + Na_2S + H_2O$. Thus, 4 g. $Na_2S_2O_4$, 2 g. NaOH and 0.4600 g. A made up to 27.9 cc. with boiled H_2O in a tube, which was then filled to the top with C_6H_6 and tightly stoppered, when warmed 8 hrs. at $60-70^\circ$ and then analyzed for NaS by a slight modification of Feld's method (*Chem. Ind.* 21, 322(1898)), gave 0.2224 g.; calcd. for the equation given above, 0.2213 g. C. A. R.

Attempts to synthesize a hydrocarbon $C_{14}H_{10}$. RICHARD MEYER, WILHELM MEYER AND KURT TAEGER. *Techn. Hochschule Braunschwig. Ber.* 53B, 2034-52(1920); cf. C. A. 11, 2803.—The present work is a continuation of the efforts, still unsuccessful,



Ph_2 in 300 g. AcOH is treated with 30 g. methylal and 150 g. concd. H_2SO_4 , the reddish soln. becomes violet after a time and there seps. a white amorphous mass which increases considerably in amt. in the course of 24 hrs. The mixt. is then gradually treated in the course of a day with 1000 g. of concd. H_2SO_4 , allowed to stand overnight and poured into much H_2O , giving a gray-white ppt. which seps. in amorphous form when attempts are made to cryst. it. Under 50 mm. it gives about 3 g. unchanged Ph_2 and at $330-60^\circ$ about 8 g. of $(\text{PhC}_6\text{H}_4)_2\text{CH}_2$, leaflets from alc., m. 159° , slowly sol. in concd. H_2SO_4 with pink color changing on warming to a dark crimson; a few particles of NaNO_2 change the bright red soln. in H_2SO_4 after a time to a deep violet. In spite, therefore, of the excess of HCHO , no A is formed. Next 2,6- $\text{Me}_2\text{C}_6\text{H}_3\text{NH}_2$ was prepd. from com. "o-xylidine" by Busch's method (*Ber.* 32, 1008(1899)), the formyl deriv. being hydrolyzed by boiling a short time with 15% HCl instead of with alc. KOH as done by B. The base was then converted into $[2,6-(\text{HO}_2\text{C})_2\text{C}_6\text{H}_3]_2$ (B) by Mayer's method (*C. A.* 5, 3690). In this connection it was observed that a clear soln. of the 2-diazoisophthalic acid could not be obtained even when the nitrite was added very slowly. The 2-iodoisophthalic ester was condensed by means of "Naturkupper" to the Me ester of B but when the B obtained from it by hydrolysis was heated in 1-g. portions with burnt lime it gave, instead of the diketone corresponding to A, only fluorenone, yellow needles from aq. alc., m. $84-5^\circ$; heated in sealed tubes with fuming HCl 3 hrs. at 150° , 180° and 200° , B was unchanged. The synthesis of $(2,6-\text{Br}_2\text{C}_6\text{H}_3)_2$ (E below) was then undertaken. 2,6,3- $\text{Br}_3(\text{O}_2\text{N})\text{C}_6\text{H}_2\text{NH}_2$ (Körner, *Jahresber.* 1875, 346), m. 202° , is obtained more quickly and in better yield (93.2%) when $p\text{-O}_2\text{NC}_6\text{H}_4\text{NH}_2$ in MeOH is treated dropwise with somewhat more than 2 mols. Br ; 300 g. in 1500 cc. alc. and 300 g. concd. H_2SO_4 treated boiling hot with 72 g. powdered NaNO_2 in small portions, boiled with frequent shaking until completely dissolved and cooled gave 200 g. 3,5- $\text{Br}_2\text{C}_6\text{H}_3\text{NO}_2$, very long, flat needles from alc., m. 106° ; 5 g. in boiling alc. treated dropwise with 4 g. NaOH in 10 g. H_2O and boiled a short time yielded 3,5,3',5'-tetrabromoazoxybenzene, yellow leaflets from PhMe , m. $196-7^\circ$. 3,5,3',5'-Tetrabromoazobenzene (164 g. from 200 g. $\text{Br}_2\text{C}_6\text{H}_3\text{NO}_2$ in 800 cc. alc. and 160 g. Zn dust treated boiling hot under a reflux with 400 cc. of 30% NaOH in small portions and heated 1 hr. longer with a small flame), golden yellow needles from PhMe , m. 244° , unchanged by boiling with As_2O_3 or AsCl_3 or with HCl in alc.; 160 g. in 1600 cc. boiling alc. and 96 g. AcOH slowly treated with Zn dust (112 g.) until completely dissolved, cooled, filtered from the excess of Zn dust and $\text{Zn}(\text{OAc})_2$ and treated boiling with much H_2O gave 135 g. of the hydrazo compound (C), almost colorless needles from $\text{EtOH-H}_2\text{O}$, m. $182-3^\circ$, reddens appreciably in the air, insol. in and unchanged by HCl , converted back into the azo compd. by treating in alc. with a little NaNO_2 , acidifying with H_2SO_4 and boiling; 3 g. boiled 2 hrs. under an air condenser with 25 cc. Ac_2O yields, together with a little of the azo compd., the N-monoacetyl derivative, needles from dil. AcOH , m. 204° ; the same result was obtained by heating 12 hrs. C is unchanged by boiling with dil. acids; long boiling with fuming HCl gives a little basic rearrangement product (0.4 g. from 0.5 g. C heated in a sealed tube at 100° with 30 cc. concd. HCl); if the temp. is raised to 150° most of the C decomps. into the azo compd. and $\text{Br}_2\text{C}_6\text{H}_3\text{NH}_2$; concd. H_2SO_4 produces the same decompn. to a large extent; 1:1 acid effects too little of the

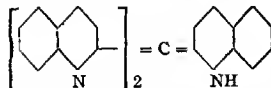
desired rearrangement; however, when to 150 cc. of a mixt. of 2 vols. H_2SO_4 and 1 vol. H_2O on the H_2O bath 5 g. C is added in small portions and the mixt. is dild. with an equal vol. of H_2O , filtered from the azo compd. (1 g.) through asbestos and satd. with NH_4OH there is obtained 4 g. 2,6,2',6'-tetrabromobenzidine (D), home-shaped crystals from dil. alc., m. 180° , assumes a faintly reddish tinge on standing, is distinctly but weakly basic, dissolves in boiling dil. acids but on cooling partially seps. as the result of hydrolysis, dissolves in concd. acids at room temp. and is partially pptd. by alkalis before complete neutralization, also by addition of H_2O ; concd. HCl satd. hot with D deposits on cooling a granular cryst. hydrochloride, obtained as a powder when HCl gas is passed into an Et_2O or C_6H_6 soln. of the D; when alc. is used as the solvent the HCl salt seps. in leaflets with 1 $EtOH$. An $AcOH$ soln. of D treated with $NaNO_2$, turns dark red-yellow, becomes turbid after a time and on heating gives a red-brown flocculent ppt. carbonizing above 300° . Diazotized in concd. HCl and coupled with β -naphthol and R salt, D gives a bright red ppt. and a dark red soln., resp. *N,N'*-Diacetyl derivative, from D gently boiled 2 hrs. with 5 parts Ac_2O , short, almost quadratic prisms from alc., m. $269-70^\circ$ (gas evolution). From 15 g. of the crude D is obtained, on treatment with C_6H_6 , 1.7 g. insol. 2,6,2',6'-tetrabromodiphenylene, $[Br_2(H_2N)C_6H_3]_2$, needles from dil. alc., m. 242° , less easily sol. in org. solvents but more easily in dil. HCl than D. Dihydrochloride, cryst. powder from Et_2O . *N,N'*-Diacetyl derivative, stout rhombic prisms from $AcOH$, m. 331° . 2,6,2',6'-Tetrabromodiphenyl (E), from 5 g. D in 100 cc. fuming HCl diazotized at 0° with 2.5 g. $NaNO_2$, added dropwise to 500 cc. boiling alc., filtered and concd., the resulting deposit of cryst. and reddish yellow resinous deposit being rubbed to a thin paste with Et_2O and spread on clay (yield, 5 g. from 49 g. D), needles from alc., octahedral crystals from Et_2O or xylene, m. 215° . The reddish brown substance formed along with the above compd. is hardly sol. in most solvents except C_6H_6 , from which ligroin ppts. it as an amorphous red powder carbonizing above 320° and having the compn. $Br_2(H_2N)C_6H_3C_6H_3Br_2N:NC_6H_4Br$ -(NH_2) $C_6H_3Br_2NH_2$ or $Br_2(H_2N)C_6H_3C_6H_3Br_2N:NNHC_6H_3Br_2C_6H_3Br_2NH_2$. On account of the poor yield of E obtained by the above method, it was attempted to brominate (p - $HO_2CC_6H_4$) $_2$ in the hope that the resulting Product on decarboxylation would give E. (p - MeC_6H_4) $_2$ was obtained in 60% yield from p - MeC_6H_4I and "Naturkuper" at 260° (Ullmann, *Ann.* 332, 44(1904)); oxidation with $CrO_2 \cdot AcOH$ converted it into a mixt. of $MeC_6H_4C_6H_4CO_2H$ and $(HO_2CC_6H_4)_2$ and subsequent treatment with alk. $KMnO_4$ oxidized it completely to the $(HO_2CC_6H_4)_2$; it was hoped that by energetic treatment 4 Br atoms might be introduced in this acid but when 2.4 g. of the acid and somewhat more than 4 mols. Br in about 15 cc. H_2O were heated 18 hrs. at $270-300^\circ$ there was obtained only a salmon-red sealing wax-like mass, very easily sol. in all org. solvents except ligroin, from which nothing cryst. could be isolated. All attempts to condense E with CH_2Br_2 and Na or with $CN_3(CO_2Et)_3$ failed; in spite of the most varied conditions the E was always recovered unchanged except that in one case where Et_2O was used as solvent there was also obtained, besides the unchanged E, a little Ph. In the presence of Cu powder, also, there was no reaction between E and CH_2Br_2 , nor between E, $(CH_2Br)_2$ and Na.

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Molecular coefficient of refraction, its additive behavior and its applicability for the determination of constitution. II. Calculation of the indexes of refraction of aromatic hydrocarbons. FRITZ EISENLOHR. Univ. Königsberg i. Pr. *Ber.* 53B, 2053-63(1920); cf. *C. A.* 15, 848.—In the present paper the aromatic hydrocarbons are taken up. From a tabulation of the values of $M \times n_D^{20}$ as given by v. Auwers (*C. A.* 14, 927) and a few other authors, E. finds the following relationships to hold. (1) The entrance of the first Me group into the C_6H_6 nucleus produces no increase (E) in the value calcd. from the sum of the atomic const. less the decrement (-21.20

units) for the aromatic nucleus union. Taking this decrement into consideration, PhMe is, therefore, optically normal. The entrance of a 2nd Me group produces an exaltation, the value of E increasing in the order p , m , o , while in tri-Me derivs. E increases in the order sym., asym., vic. (2) The difference between the values of E for the o - and p - and the vic. and sym. isomers, resp., is $0.5 \times$ the no. of side chains (*i. e.*, 1 for the di- and 1.5 for the tri-Me compds.). The values of E for the p - and sym. compds. are to those for the m - and asym. isomers, resp., as 0.7:1.0. (3) The influence of a Me group as a side chain on the E value differs from that of other groups (Et, Pr, etc.), which give values of E higher by about 0.3 unit. (4) The increase in E with the introduction of side chains into the nucleus is quite regular; the introduction of a Me group into the o -position to a side chain already present produces an increase of 1.35 units while its entrance between two side chains in the 1,3-positions causes an increase of 2.35 units, and introduction into a di- m -position (position 5 in a compd. already substituted in positions 1 and 3) gives an increase of 0.80 unit. C. A. R.

Di- and triquinolylmethanes joined through the pyridine nuclei. I. *sym*-Triquinolyl-2-methane. GÜNTHER SCHEIBE AND ERNST ROSSNER. Düsseldorf Akad. f. Med. und Univ. Erlangen. Ber. 53B, 2064-9 (1920).—When equimol. amts. of 2-chloroquinoline (A) and quinaldine (B) are heated in the presence of B.HCl, the liquid begins to become red-brown at 170° and after being heated 30 min. at 220° solidifies to a cryst. mass on cooling. It is then dissolved in alc., made alk. and freed of unchanged A and B with steam, leaving a red-brown resin sol. in Et₂O and C₆H₆; from this soln. dil. acid successively removes two products of markedly differing basicity. The more strongly basic compd. (*sym*-diquinolyl-2-methane) gives with the acid a wine-red dye, which, however, is decolorized by an excess, while the more weakly basic compd., *sym*-triquinolyl-2-methane (C), retains its red color in strong acid. If 2 mols. A are used to each mol. B and the mixt. is heated to the b. p. of the B vigorous ebullition suddenly sets in and the mass solidifies to a resin with green luster which contains only C (yield 70%). It seps. from alc., C₆H₆, Et₂O, Me₂CO and C₆H₅N in fine, faintly reddish needles becoming pure white on long standing, sepg. from concd. HCl on diln. with a little H₂O as the *dihydrochloride*, C₂₁H₂₁N₂Cl₂, prisms with green luster, decomp. about 300°. *Dipicrate*, brown-red prisms with greenish surface luster, decomp. 212°. *Perchlorate*, decomp. 242°. The free C reddens 160°, m. 199-200°, mol. wt. in boiling C₆H₅N 389-400, sol. without color in alc. but the soln. quickly becomes yellow-red on warming and the color is intensified by addition of a little alkali. C₆H₅N also dissolves it with yellow-red color. Evapu. of these solns. gives the original colorless needles, pointing to an equil. between a colored and a colorless form. This is indicated even more clearly by the absorption spectrum of the colored solns., which show 2 bands with max. at about 523 and 487 μ . These same bands, although considerably more intense, are obtained when very little acid is added; on addition of more acid they coalesce into a broad band, which is not further changed by an excess of acid. If, now, a little Et₂O is added to this soln. and it is quickly made alk. with KOH the hase seps. in an intensely brick-red form remaining as micro-leaflets when the Et₂O is driven off; on attempted crystn. it goes over into the colorless form, also when allowed to stand some weeks. The red form is assigned the structure

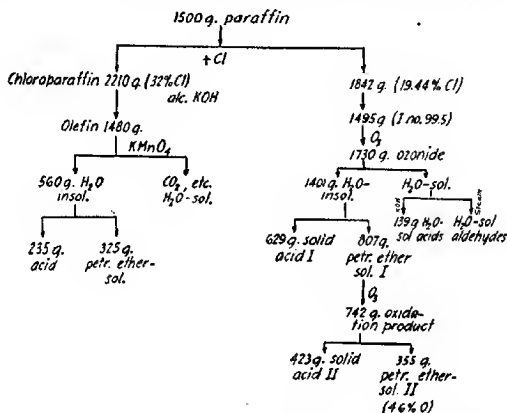


With excess of MeI at 100°, 1 g. C gives 1.15 g. of a compound, C₂₁H₂₂N₂I, dark red prisms m. 245° (evolution of MeI), regenerates C with alkalis. Heated 36 hrs. at 100° with MeI and alc., C gives a compound, C₂₁H₂₂N₂I₂, m. about 300°. Neither of these compds.

can be recrystd. Acetylation in the ordinary way likewise does not show the presence of a sec. N atom in C. Attempts to prep. a nitrosamine by treating C in AcOH with NaNO_2 gave a colorless compound sepg. from $\text{C}_8\text{H}_{17}\text{N}\cdot\text{Et}_2\text{O}$ in needles, decomp. 192° , also obtained from C in aq. alc. suspension with HNO_3 , sol. in concd. H_2SO_4 with green color changing on diln. to the color of C in dil. acids, very unstable, quickly becoming brownish, especially in the light; its compn. is $\text{C}_{23}\text{H}_{41}\text{O}_2\text{N}_4$ (N, 12.42–12.56%). On the other hand, the presence of H on the central C atom of C can be established. Mild oxidizing agents, like H_2O_2 , convert C into *triquinolyl-1-carbinol* (obtained in good yield by allowing C to stand in alc. with a trace of acid until decolorized), prismatic crystals m. 168° , insol. in and giving no color with dil. acids, sol. in concd. H_2SO_4 with faint blue fluorescence changing to strong yellow-green fluorescence on boiling, forms no methiodide in sealed tubes; *picrate*, $\text{C}_{23}\text{H}_{41}\text{O}_8\text{N}_3$. CHAS. A. ROUILLER

Preparation of oxidation products of paraffin. I. ALFRED SCHAARSCHMID. AND MAX THELE. Techn. Hochschule, Berlin. *Ber.* 53B, 2128–43 (1920).—S. and T. "opened" the paraffin mol. by chlorinating it, split off HCl from the chlorinated product and oxidized the resulting olefin mixts. The Cl was passed into the melted paraffin at 160° through a Witt stirrer, which was rapidly rotated, thus finely dividing the current of gas. The reaction is almost complete and proceeds without the aid of external heat. The Cl could be removed again quant. as HCl by heating the products to about 300° ; the olefins so obtained have a materially lower I no. than those obtained with alc. KOH at lower temps. The methods for oxidizing paraffin itself with O which have become known since the present work was done lead always to a profound demolition of the mol. with formation of fatty acids and other oxidation products (cf. Bergmann, *Z. anorg. Chem.* 31, 69); S. and T., by the process described in the Swiss pat. 49,488, Kl. 12 o, of the Chem. Fabr. Troisdorf, by which it is claimed that 70% of the paraffin can be converted into oxidation products, obtained 45% of fatty acids. They carried out their oxidation expts. on the more or less unsatd. olefins obtained as stated above. First they attempted to split the chains with KMnO_4 at the double bonds. From an olefin with a Br no. of 20.4 (obtained from a chloroparaffin with 10.6% Cl by means of alc. KOH) they were able to isolate the Ag salt of an acid $\text{C}_{14}\text{H}_{25}\text{CO}_2\text{H}$. The more strongly unsatd. paraffins show a much greater and quicker absorption of O. The olefin obtained with alc. KOH from a chloroparaffin with 32% Cl was oxidized in 2 ways. The case with which all these H_2O -insol. unsatd. hydrocarbons are oxidized depends greatly on the state of their subdivision. Na palmitate in H_2O is but little affected by KMnO_4 but such a soln. has a very pronounced ability to hold neutral oils in suspension and it was found that the very stable suspension of the olefin in an aq. Na palmitate soln. of a definite strength on treatment with KMnO_4 quickly takes up O, the max. being reached after addition of about 6 parts KMnO_4 . As in the oxidation itself soaps are formed. In a 2nd expt. S. and T. started with a little olefin in a little Na palmitate and more olefin was added as the KMnO_4 was used up. Assuming that the palmitic acid is not materially changed there were obtained in the 2 expts. about the same amts. of "crude acid" (mixt. of saponifiable and unsaponifiable material). The 2 "crude acids" also contained about the same amts. of unsaponifiable material and, therefore, of fatty acids, but the acid no. of the product obtained in the 2nd way was higher. The resp. yields from 140 g. olefin in the 2 expts. were as follows: crude acid insol. in H_2O 56 g. (acid no. 164), 53 (acid no. 225); unsaponifiable material 26.2, 30.4; acid no. after removing unsaponifiable material 226, 297. The oxidation with KMnO_4 apparently does not stop at the stage of splitting at the double bonds but further changes a large part of the cleavage products. It is, moreover, probable that a considerable part of the cleavage products consists of H_2O -sol. acids which on acidification of the soap soln. remain in soln., but nevertheless much of the olefin is oxidized,

in part to CO_2 , as there is a copious evolution of CO_2 on acidification. The oxidation of the double bonds with O_3 by Harries' method was also applied by S. and T. to their olefins. The addition of the O_3 proceeds easily, the amt. added corresponding closely to the amt. of HCl split off in prep. the olefin. The ozonides were decompd. with H_2O and the non-acid aldehydic parts reoxidized with O_3 . From 150 g. olefin (obtained with alc. KOH from a chloroparaffin with 19.4% Cl) was obtained 105 g. of higher fatty acids, together with large amts. of lower, H_2O -sol. acids. The results of the expts., which are described in detail, are summarized in the following scheme:



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Constitution of acetatomercuriformic ester. Reply to W. Manchot. WALTER SCHOELLER. Univ. Berlin. *Ber.* 53B, 2144-7(1920); cf. *M.*, *C. A.* 14, 3416.—S. maintains the correctness of his views as against those of M. C. A. ROUILLER

The montan wax of the lignite of Central Germany. R. PSCHORR AND J. K. PFAFF. Techn. Hochschule Berlin-Charlottenburg. *Ber.* 53B, 2147-62(1920).—The object of the present work was to det. the mol. wt. of the alcs. in the wax and to isolate them as chem. individuals. The crude wax (A) from the Riebec Montan Works was extd. in a Soxhlet successively with Et_2O and Me_2CO until the exts. were almost colorless (4-5 hrs.). The yields in 2 such extns. were: Et_2O ext. (B) 39.5, 30.8; Me_2CO ext. (C) 12.1, 22.6; residue (D) 48.4, 47.3%. A, B, C and D showed the following const., resp.: acid no. 22.7, 34.3, 67.7, —; ester no. 36.7, 29.2, 32.4, 43.4; sapon. no. 59.4, 63.5, 100.1, 43.4; acetyl sapon. no. —, 68.9, 101.7, 43.6; I no. 13.9, 23.0, 17.2, 7.0. Most of the free acid is, therefore, in B and C (especially C); D is free of unesterified acid and rich in esters. Further extn. of the residue with Me_2CO for 4 hrs. removed 3% more with an acid no. of 0 and sapon. no. of 43.5; no attempt at exhaustive extn. was made. B, C and D were separately sapond. with alc. KOH in the presence of C_6H_6 , the K soaps converted with CaCl_2 into the Ca soaps and the latter exhaustively extd. with Me_2CO , with the following results for A, B, C and D, resp.: % of alcs. + unsaponifiable material 26, 21, 22, 31; acetyl sapon. no. of alcs. 130, 133, 132, 127; mean mol. wt. of alcs. 389, 379, 382, 399. Acetylation of the "alcs. + unsaponifiable matter" by heating with Ac_2O and subsequent crystrn. from alc. effects a complete sepn. of the acetylated aliphatic alcs. from the unsaponifiable matter and resin alcs. as the aliphatic acetates

are considerably more sol. than the other components. Isolation of the alcs. was effected most easily from D; after its sapon. the neutral part formed an almost colorless wax consisting of the pure alcs., m. 80-2°; these could not be sepd. by fractional crystn. but fractionation of the acetates from Et₂O-EtOH (1:1) yielded 3 fractions, m. 59°, 65° and 70°, with sapon. nos. of 144, 133 and 117 and sapond. by alc. KOH to *tetracosanol* (E), C₂₄H₄₈O, ceryl and myricyl alcs., m. 83°, 79° and 88° (yields, 0.5, 3 and 3 g. acetate, resp., from 10 g. of the mixt.). The 3 alcs. were similarly isolated from B and C, B yielding chiefly E and ceryl alc., C almost pure ceryl alc. The Ca salts, after the extrn. with Me₂CO, were decompd. with concd. HCl in the presence of some C₆H₆ and the crude montanic acid (F) was freed of resinous impurities by esterifying with EtOH and H₂SO₄ or HCl gas, the Et ester of F being considerably more sol. in alc. than the esters of the resinous compds. The acid portions of B, C and D all yielded the pure Et ester of F, m. 66.5°, which on acid hydrolysis gave F, m. 83.5°, mol. wt. 426 (titration). The pure F was most easily obtained from C. As a result of their work, P. and P. conclude that their A contained 17% free F (max.), 53% esters of F and a minimum of 30% of substances of unknown compn. In preliminary expts. the true montan resin, sol. in cold alc., was isolated from B by Schneider's method (*Ges. Abh. z. Kenntnis d. Kohle* 1918 [3], 225); slow evapn. of the alc. soln. yielded a small amt. (0.8 g. from 500 g. A) of prisms m. 241° after 10 crystns. from C₆H₆, with 81.26% C and 9.81% H, corresponding approx. to C₂₄H₄₈O₂, reacts neutral, has a sapon. no. of 0 and an I no. of approx. 54.

CHAS. A. ROULLER

Physical structure of some organic compounds of high molecular weight. Preliminary communication. I. R. O. HERZOG AND WILLI JANCER. Kaiser-Wilhelm-Inst. f. Faserstoff-Chem., Berlin-Dahlem. *Ber.* 53B, 2162-4 (1920).—Applying Debye and Scherrer's Röntgen-spectrographic method (*Nachr. kgl. Ges. Göttingen* 1918, 18) H. and J. find that cotton (0.03% ash), crimped and pressed in a capillary into a rodlet, shows interference bands corresponding to the rhombic system of crystals and an axial ratio of 0.6935:1:0.4467; exactly the same results were obtained with ramie (0.03% ash) and wood cellulose (0.1% ash). In order to test whether these fibers have a regular structure along the axis bundles of parallel (instead of crimped) ramie and flax fibers were illuminated. The interferences do not form lines as in the D. and S. method hut groups of 4 points lying at the corners of rectangles whose centers are the points of penetration of the Röntgen rays. The cellulose fiber is to a certain extent comparable with a thread-shaped tungsten crystal. Lignified cellulose, crimped jute (0.5% ash) and linden wood powder (0.7% ash) give pictures differing from those of cellulose only within the limits of error of the measurements. Crimped artificial silk fibers (0.02% ash) and powdered viscose gave interference bands different from those of cellulose but showing that the cryst. structure is still preserved. Unlike cellulose, however, parallel fibers give not a punctiform interference hut concentric circles, i. e., the same picture as when crimped. Artificial silk from acetylcellulose (0.08% ash) proved to be amorphous. Starch from rice (0.6% ash), maize (0.03% ash) and wheat (0.6% ash) showed identical interference bands corresponding to the rhombic system and the axial ratio 0.7252:1:0.5509, and glycogen (2% ash) proved to be amorphous, as did also human hair (2.6% ash) and wool (0.9% ash). Debasted silk (1.5% ash) and tussah silk (0.7% ash) unexpectedly showed interferences, both when crimped and in parallel fibers.

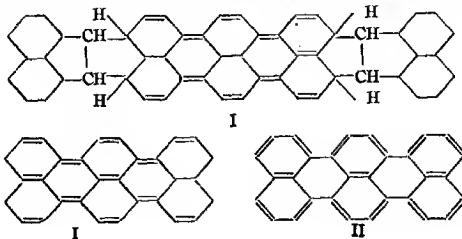
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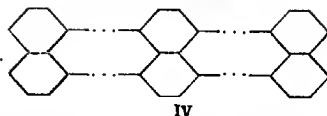
Three new peculiar hydrocarbons: leucacene, rhodacene and chalcacene. KAROL DZIEWONSKI, with J. PODGÓRSKA, Z. LEMBERGER AND J. SUSZKA. Univ. Kraków. *Ber.* 53B, 2173-92 (1920); cf. *C. A.* 12, 2564.—Acenaphthene (A) on pyrogenic distn. easily loses H, forming chiefly acenaphthylene (B), C₁₀H₈.CH:CH₂, hut there are also

formed various other compds., including 3 hydrocarbons, *leucacene*, *rhodacene* and

chalcacene which are believed to have the structures, I, II and III, resp. II and III are thought to result from A losing its $-\text{CH}_2\text{CH}_2-$ grouping and the *peri*-H atoms of the C_{10}H_8 nucleus with the formation of bi- or quadrivalent, quinoid or benzoid naphthalene residues (IV) which, depending on the conditions of temp. and pressure, combine to form the labile naphthoquinoid or the stable naphthoid *peri*-dinaphthylene-naphthalene (II and III, resp.). The formation of I may be considered as a kind of thermopolymerization of 2 mols. B with 1 mol. II. The name *leucacene* has been adopted for I in view of its lack of color and of its origin and, in agreement with Fleischer, the name "pyracene" which was formerly assigned to I is reserved for the hypothetical mother substance of the quinone prepd. by him. (C. A. 14, 3249). More accurate methods have shown also that the empirical formulas $\text{C}_{24}\text{H}_{14}$ and $\text{C}_{24}\text{H}_{12}$ formerly assigned to I and III are incorrect. The pyrogenic distn. of the A is carried out as quickly as possible, in CO_2 , in a long wide quartz tube lined with Fe or Cu wire heated to redness; the receiver, a long-necked flask, is further connected with 2 cumene wash bottles. If it is desired to isolate the B it is extd. from the red-brown distillate with alc., then with cold and hot C_6H_6 and finally with xylene or cumene. To obtain I in the best possible yield, however, it is advisable to ext. at once with cold C_6H_6 , without regard to the B, as long as the dark red products dissolve. The ext. is treated with a little ligroin to turbidity, a red-brown, somewhat resinous ppt. sepg. after a time. The filtrate is repeatedly allowed to conc. somewhat and the deposits formed are collected. After thorough washing with hot alc. and cold C_6H_6 and repeated crystn. from C_6H_6 , they yield the pure I as a voluminous silky substance, m. 250° . The C_6H_6 mother liquors from the crude I are evapd. to dryness and the residue is extd. with alc., which dissolves the A + B, the B then being sepd. from the A through its difficulty sol. picrate; the yield of pure B is about 60% of the original A, about 25% of which is recovered unchanged. The residue, after the extn. with alc., is treated with cold C_6H_6 and the dark red ext. treated with much ligroin, which gives a voluminous red-brown ppt. consisting chiefly of polyacenaphthylene (C) and some " β -chromacene" (D) (see below), while the Bordeaux-red " α -chromacene" (E) remains largely in soln. The ppt. is washed several times with boiling ligroin and extd. with hot Me_2CO , which dissolves the orange-red D. On evapn. and long standing the ligroin and Me_2CO exts. deposit D and E. C is obtained in pure, almost colorless form by repeated soln. in C_6H_6 , boiling with charcoal and pptn. with ligroin or alc. The products insol. in cold C_6H_6 are successively extd. with hot C_6H_6 , xylene and cumene, which dissolve the rest of the I, II and III, together with traces of "chromacene" fractions which have not yet been investigated. The individual hydrocarbons are sepd. by fractional crystn. from C_6H_6 ; the isolation of the II offers the greatest difficulty on account of its instability and its relatively small tendency to cryst. After the isolation of the III, by extn. of the difficultly C_6H_6 -sol. residues with cumene and PhNO_2 , there still remains a very difficultly sol. dark brown carbonaceous mass, which is extd. with hot PhNH_2 ; the resulting red-brown soln. with olive-yellow fluorescence deposits on cooling and evapn. a brown-black or almost wholly black substance provisionally designated as " γ -chromacene" (F). I on drying in the air soon becomes covered with a superficial light reddish or pink layer, seps. from C_6H_6 , xylene and other hydrocarbons in flat needles or elongated tablets, from PhNO_2 in light yellow elongated crystals, sol. with partial change in the higher boiling solvents (PhNO_2 , cumene, C_{10}H_8). If the C_{10}H_8 soln. is heated a long time it becomes bluish red, then orange. It dissolves in cold concd. H_2SO_4 with violet-red color soon changing to gray-violet. On crystn. it forms solvates, especially with C_6H_6 from which it seps. with about 12%, which it loses at $100-20^\circ$, becoming covered with a reddish or pink layer. In a capillary it begins to turn pink 120° , becomes dark red 210° , reddish violet 220° , m. $250-2^\circ$ with red color. On long heating in the air it changes distinctly (at about 150°) with increase in wt. and formation of an amorphous

brownish red mass containing O and consisting of C, III and substances similar to the chromacenes. Under diminished pressure I suddenly decomps. about 175° into B and II. Finally when a soln. in a high boiling solvent (PhNO₂) is boiled some time, it becomes bluish red, then orange or orange-red, II being at first the chief product of the rearrangement and passing into III as the boiling is continued. I crystd. from C₆H₆ behaves like a typical compd. of high mol. wt.; it becomes strongly electrified on rubbing. A cold dil. soln. treated with Br becomes fiery red, then blue and finally violet-black and deposits a violet-black ppt.; only during the last stages of the bromination is any HBr evolved. A cold PhNO₂ soln. treated dropwise with concd. HNO₃ becomes blue-green, then olive-green and finally olive-black and forms a violet-black ppt. CrO₃ in AcOH or H₂SO₄ rapidly oxidizes it to naphthalic acid and a brown-yellow amorphous acid substance. I gives a mol. wt. of 711 in boiling (CH₃Br)_n, 672 in PhNO₂. Pure II is best obtained by boiling a 4-5% soln. of pure I in PhNO₂ 10-2 min., cooling, filtering off the cryst. mixt. of I and III which seps., removing the excess of PhNO₂ from the filtrate *in vacuo*, pptg. with alc. and removing the last traces of I and III by crystg. from xylene, from which the I and III sep. first. It forms a dark violet cryst. mass with greenish metallic luster somewhat similar to Me violet, m. 338-40°, changes into III on long heating in high boiling solvents (especially PhNO₂), sol. in concd. H₂SO₄ with blue-violet color. Its solns. in C₆H₆ or xylene have a pure red color with bluish tinge in transmitted light and a bright brick-red fluorescence in reflected light; dil. solns. in C₆H₆ or its homologs show 4 absorption bands at λ 575-555, 535-510, 495-475 and 460-445 μ . It isomerizes almost instantly into III on strong illumination of its dil. solns. but unilluminated solns. show not the slightest change in color or spectrum even on long standing. Its mol. wt. in freezing C₆H₆ is 376. III, isolated from the pyrogenic distn. products of A as described above, or by heating I 0.5 hr. at 206-10° in PhNO₂, forms Bordeaux-red flat needles or tables with bronzeluster, m. 358-60°, sol. in concd. H₂SO₄ with cherry-red color, shows in dil. solns. a yellow color and orange fluorescence, in concd. solns. an orange color and a bronze-red fluorescence; the absorption spectrum contains 2 bands at 565-535 μ and 525 μ to the ultraviolet. III is oxidized with relative difficulty and on long treatment with CrO₃ gives chiefly an acid brown-red amorphous substance. Its mol. wt. in boiling PhNO₂ is 361-92. C, C₂₄H₁₂ or (C₆H₄)_n, is an amorphous, almost colorless powder, m. above 330°, easily sol. in cold C₆H₆ with light yellow color, difficultly in cold concd. H₂SO₄ with olive-green color. E is a dark red microcryst. powder, sinters 190°, m. 240°, relatively difficultly sol. in cold concd. H₂SO₄ with dark gray-violet color; dil. C₆H₆ or ligroin solns. have a pure yellowish red color and yellow fluorescence and on illumination quickly change to a brownish red. E contains about 93.5% C and 4.9% H. D, a microcryst. brownish red substance, sinters 240°, m. about 265°, sol. in C₆H₆ with wine-red color and orange-yellow fluorescence, contains 93% C and 5.2% H. F is a black powder, m. above 400°, sol. in traces in boiling cumene with red-brown color and olive-yellow fluorescence, more easily in PhNO₂ and PhNH₂ with dark brown color, in hot H₂SO₄ with violet-black color, contains





about 92.9% C and 4% H.

CHAS. A. ROUILLER

Dimethyldiacetonealkamine and dimethyldiacetoneamine. HANS ROLFS. Univ. Freiburg i. B. *Ber.* 53B, 2203-6(1920).— $\text{Me}_2\text{NCMe}_2\text{CH}_2\text{CH}(\text{OH})\text{Me}$ (A), mobile liquid of narcotic odor, b_n 75–83°, is obtained in 4.4-g. yield from 5 g. $\text{H}_2\text{NCMe}_2\text{CH}_2\text{CH}(\text{OH})\text{Me}$ (B) heated 6 hrs. at 120–5° with 7.2 g. of 40% HCHO , 3.8 g. HCO_2H and 10 g. H_2O , treated with 5 g. NaOH in 10 cc. H_2O , extd. with Et_2O and dried with potash. Benzozate (1.6 g. from 2 g. A and 3 g. BzCl by the Schotten-Baumann method), thick oil, b_n 175–80°. When 3.5 g. A in 40 cc. AcOH at 92° is slowly treated, with turbinig, with 2 g. CrO_3 in 15 cc. AcOH , heated after 45 min. for a short time to 100°, evapd. *in vacuo* to a sirup, made alk. at 0° with 30 g. KOH in 30 cc. H_2O , extd. 15 hrs. with Et_2O , dried and cautiously freed from Et_2O at 40° and of the last traces *in vacuo* at room temp. there is obtained 2 g. of dimethyldiacetoneamine (C), unstable oil of narcotic odor; *oxime*, crystals from Et_2O , begins to sinter 35°, slowly m. up to 44°; *picrate*, m. 154–5°. Hess' "dimethyldiacetoneamine," $\text{C}_8\text{H}_{17}\text{ON}$, which be obtained from B with excess (3 mols.) of HCHO without HCO_2H (C. A. 10, 467), is, therefore, entirely different from C and must be an isomer of the latter; possibly it has the cyclic structure $\text{MeN.CMe}_2\text{CH}_2\text{CHMe.O.CH}_2$.

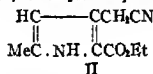
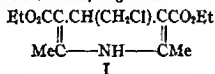
CHAS. A. ROUILLER

Anomalous aniline salts. HJ. MANDAL. Univ. Upsala. *Ber.* 53B, 2216-8 (1920).—Of the considerable number of "anomalous ammonium salts" known only a very few are salts of simple, O-free amines. It is, therefore, of some interest that PhNH_2 also forms anomalous salts. When M., in order to prep. anilinochromic compds., heated sublimed CrCl_3 with PhNH_2 , he obtained, on allowing the green soln. to stand, a cryst. mass whose compn. was not always the same but which could always be represented by the formula $[\text{CrCl}_2(\text{PhNH}_2)_4]\text{Cl} + n\text{PhNH}_2\cdot\text{HCl} + n\text{PhNH}_2$, which is best explained by assuming the presence of an anomalous aniline hydrochloride, $(\text{PhNH}_2)_2\cdot\text{HCl}$. Such a salt is easily obtained by dissolving $\text{PhNH}_2\cdot\text{HCl}$ in warm PhNH_2 ; on cooling it seps. in fine needles which slowly lose PhNH_2 at 17–8° (Cl after 4 days 17.2%), and dissolve in H_2O with sepn. of PhNH_2 droplets. When 2 parts $\text{PhNH}_2\cdot\text{HCl}$ are treated with about 1 part PhNH_2 , the liquid mixt. solidifies in a few min. to a hard mass. From a soln. of $\text{PhNH}_2\cdot\text{HI}$ in PhNH_2 satd. at 100°, nothing crystd. at temps. above the f. p. of PhNH_2 , but an impure anomalous hydrobromide was obtained by satg. PhNH_2 at 100° with $\text{PhNH}_2\cdot\text{HBr}$; on cooling to 4° there crystd. a substance which, dried some hrs. at 10°, contained 10.8–11.5% Br; calcd. for $(\text{PhNH}_2)_2\cdot\text{HBr}$, 10.68.

CHAS. A. ROUILLER

A synthesis of pyrrole compounds from dihydropyridine derivatives. ERICH BENARY. Univ. Berlin. *Ber.* 53B, 2218-24(1920).—When 10 g. I (C. A. 12, 2568) and 10 g. powdered KCN are heated 5 hrs. under a reflux in 25 cc. alc., cooled and dild. with H_2O there seps. a heavy oil which soon solidifies to a yellowish cryst. mass (about 9 g.), sepd. by fractional crystn. from strong alc. into the less sol. diethyl 4'-cyanodihydrocollidinedicarboxylate (A) (I with CN instead of Cl), leaflets, m. 106–7°, and [2-methyl-5-carboxyethylpyrrol-4]-acetonitrile (II), best obtained by boiling the above crude product a short time with alc. KOH , evapg. on the H_2O bath and treating with H_2O , whereby all the A present is completely converted into II; the II seps. from alc. or C_6H_6 in soft needles, m. 150°, does not give the pine-splinter reaction; it is formed

in 70% yield from pure A boiled a short time with alc. KOH. Free acid (B), from II boiled several hrs. with alc. KOH, microneedles from AcOH, turns brown 250°, decomp. about 284°; if it is boiled 12 hrs. under a reflux with 12 parts Ac₂O, cooled and poured into ice-cold soda it yields the mixed *acetic anhydride*, C₁₈H₁₉O₅N₃, 4-sided prisms from CHCl₃, m. 149–50°, immediately resolidifies, turns brown about 250° and carbonizes about 290°, regenerates B on standing in alc. or in contact with NH₄OH; *in vacuo* at 180–80° it loses AcOH and yields a solid gray mass, which, after boiling up with CHCl₃, washing with dil. NH₄OH and extg. with AcOEt, begins to turn brown about 260°, completely decomp. about 290° and has the compn. of the normal *anhydride*, C₁₈H₁₇O₅N₃, of B. [2-Methylpyrrol-4]-acetonitrile, obtained by distg. B mixed with 2 parts KOH, needles from EtOH-H₂O, m. 87–9°, colors a pine splinter moistened with HCl an intense red-violet; it is also obtained by distg. B alone or with sand. If the nitrile is well mixed with powdered KOH and distd., it gives H₂O, NH₃ and 2,4-dimethylpyrrole. 5,5'-Methylene-bis-[2-methylpyrrol-4-acetonitrile], from 1 g. of the nitrile allowed to stand some time with 1 cc. HCHO soln. in alc. and 2 drops concd. HCl, needles from alc., begins to turn brown 310°, decomp. completely about 330°.



does not give the pine-splinter reaction.

CHAS. A. ROUILLER

Halogen bound to the ring carbon atom and its replacement by other substituents.
II. Replacement of the halogen by OH, SH, SeH. KARL W. ROSENEMUND AND HERBERT HARMS. Univ. Berlin. *Ber.* 53B, 2226–40(1920); cf. *C. A.* 14, 1546.—The ring halogen can be replaced by OH by the action of alkalis or the neutral salts of weak acids in the presence of Cu. As the prepn. of phenols from halogen compds. and alkalis has been described in various publications, especially in the patent literature, only the results obtained with neutral salts are given in the present paper. The reaction proceeds according to the general equation $\text{PhX} + \text{AcOM} = \text{PhOAc} + \text{MX}$. In the course of the reaction the phenol esters are hydrolyzed, the mixt. becomes acid and the reaction finally comes to a standstill but immediately starts up again when the excess of acid is neutralized with alkali, and can be thus carried to completion. If the reaction is carried out in sealed vessels, CaCO₃ is added to neutralize the acid; NaOAc and borax also were used. In an anhydrous solvent (a mixt., m. 226°, of 2 g. KOAc and 1.4 g. NaOAc), the halogen is also completely removed but the reaction proceeds further. Thus, when 1.5 g. *o*-ClC₆H₄CO₂K and some Cu bronze are heated 5 hrs. at 245–55° in the KOAc-NaOAc mixt. there is a 70% replacement of the Cl, as shown by the Volhard titration, and the Et₂O ext. of the acidified soln. of the reaction product yields on evapn. *o*-PhOC₆H₄CO₂H. *o*-ClC₆H₄CO₂K (5 g.) heated 9–10 hrs. at 140–50° in sealed tubes with 7 g. NaOAc and 0.5 g. Cu(OAc)₂ in 20 cc. H₂O gives 3.2 g. of a mixt. of unchanged ClC₆H₄CO₂H and of *o*-HOC₆H₄CO₂H; a sepn. of the two by boiling with excess of milk of lime indicated that the yield of HOC₆H₄CO₂H was about 83%. In an expt. with 3.5 g. ClC₆H₄CO₂H and 7 g. crystd. borax, the mixed acids m. 120.5–1.0° and the yield of HOC₆H₄CO₂H was only 55%. When 1 g. *o*-BrC₆H₄CO₂Na, 1.2 g. β-C₁₀H₇SO₃Na and a little "Naturkupfer C" are heated under a reflux with occasional neutralization with soda, the Br is practically quant. removed in about 4 hrs. and on diln. with H₂O, filtration and acidification *o*-HOC₆H₄CO₂H seps. Without Cu, Br can be detected only in traces after 14 hrs. boiling. PhBr (5 g.), 6 g. crystd. NaOAc, 0.5 g. CaCO₃, 0.5 g. Cu(OAc)₂, 10 cc. H₂O and 15 cc. alc. heated about 15 hrs. at 220–40° and 5 hrs. at 270–80° gave 1.5 g. PhOH, while from 10 g. PhBr, 14 g. crystd. borax, 0.8 g. Cu(OAc)₂, 20 cc. H₂O and 15 cc. alc. heated about 12 hrs. at 230–40° and 1 hr.

at 260–70° was obtained 1.5 g. PhOH. The replacement of the halogen by S was tried out with thiocyanates. PhBr (10 g.), 9 g. CuSCN and 40 cc. C₆H₅N dried over BaO, when heated 8–9 hrs. at 180°, freed from most of the C₆H₅N by distn., and from the rest by rubbing with 10% HCl, extd. with Et₂O, dried and fractionated, gave 0.9 g. PhCN (0.6 g. more was obtained on extn. with Et₂O of the C₆H₅N distillate neutralized with HCl) and 2.7 g. of a yellowish oil, b₁, 175–95°, solidifying in the condenser and yielding, on crystn. from alc., needles, m. 60–1°, of Ph₂S₂; the yellow mother liquors from the Ph₂S₂, containing Ph₂S₂ (Hinsberg, C. A. 4, 2808), were heated with Zn dust and 25% HCl as long as H₂S was evolved, filtered and poured into H₂O and the resulting oil was taken up in CHCl₃, shaken with NaOH, sepd. from the CHCl₃ (the last traces of which were removed with Et₂O), acidified with dil. H₂SO₄, extd. with Et₂O, treated with alc., freed from the Et₂O on the H₂O bath, treated with alc. NH₃ and allowed to stand overnight, yielding crystals of Ph₂S₂, probably formed by oxidation. The CHCl₃ ext. of the alk. soln. yielded an aromatic oil, identified as Ph₂S by its conversion in AcOH with Br into (*p*-BrC₆H₄)₂S, leaflets from alc., m. 112–2.5°. When the fractionation of the product was done *in vacuo*, not much Ph₂S₂ was formed hut under atm. pressure such was not the case; the undecompd. Ph₂S₂ could be sepd. from the oily Ph₂S₂ by freezing out. Yield of PhCN 23, of Ph₂S 39%. In the above reaction the PhSCN first formed rearranges into PhNCS, which is then desulfurized to PhCN. This can be isolated only when working in C₆H₅N; in aq. alc. the PhSCN with the excess of H₂O forms PhSH + CO₂ + NH₃ and the PhSH either is oxidized to Ph₂S₂ or, reacting with unchanged PhBr, gives Ph₂S. The process is further complicated by the fact that on long heating at high temps. aromatic disulfides decomp. according to the equation 2R₂S₂ = R₂S₂ + R₂S. From 8 g. *p*-BrC₆H₄Me, 5 g. CuSCN, 40 cc. C₆H₅N and 2 cc. H₂O heated about 12 hrs. at 220° and 1 hr. at 250° are obtained a fraction b₁ 110–20° (*p*-MeC₆H₄CN) and 2 fractions b₂ about 160° and 170–90°, depositing in a freezing mixt. needles, m. 56–7°, of (*p*-MeC₆H₄)₂S; the oil drained from these and worked up as above yielded *p*-MeC₆H₄SH, m. 42.5–3.0°, and (*p*-MeC₆H₄)₂S₂, m. 46°. (MeC₆H₄)₂S₂ could not be isolated in solid form. *o*-BrC₆H₄Me (10 g.), 6 g. CuSCN and 40 cc. C₆H₅N heated 10 hrs. at 195–210° gave 22% *o*-MeC₆H₄CN, 44% (MeC₆H₄)₂S₂ and (MeC₆H₄)₂S. From 5 g. *o*-ClC₆H₄CO₂K, 3 g. CuSCN and 40 cc. C₆H₅N heated 5 hrs. at 140–50° was obtained (*o*-HO₂CC₆H₄)₂S. *o*-BrC₆H₄CO₂H reacts more readily; 5 g. in 50 cc. of 0.5 N NaOH boiled under a reflux 4.5 hrs. with 4 g. KSCN and "Naturkupfer" gives 3 g. (crude) (*o*-HO₂CC₆H₄)₂S₂. *p*-BrC₆H₄CO₂H does not react so readily, being practically unchanged after 15 hrs., hoiling under a reflux; when 4 g. in NaOH is heated 6 hrs. at 160–70° and 8 hrs. at 180–200° with 5 g. KSCN, 1 g. CuSCN and 0.5 g. BaO₂ (to provide O) (HO₂CC₆H₄)₂S is formed; in another expt. where 6 g. of the acid in 32 cc. N KOH was heated 15 hrs. at 195–210° with 7.5 g. KSCN, 1.5 g. CuSCN and 0.7 g. BaO₂ and the product was extd. with Et₂O, there was obtained 0.35 g. Ph₂S₂. α -C₁₀H₇Br (4 g.), 2.5 g. CuSCN, 25 cc. C₆H₅N and 1 cc. H₂O heated about 7 hrs. at 160–80° and about 10 hrs. at 180–95° yielded (α -C₁₀H₇)₂S. From 5 g. 2-bromoanthraquinone, 4 g. KSCN, 2 g. CuSCN, 35 cc. alc. and 10 cc. H₂O heated about 10 hrs. at 195–205° was obtained a good yield of dianthraquinonyl 2-sulfide, felted needles from PhNO₂, m. 289.5° (Ullmann-Goldberg, Ger. pat. 233,591, gives 275–6°), sol. in cold concd. H₂SO₄ with violet-red color, reprecip. by H₂O. When 8 g. *o*-BrC₆H₄CO₂Na, 4.5 g. KSeCN, 0.1 g. Cu bronze and 40 cc. H₂O are heated 8 hrs. at 150°, filtered from the Cu₂Se, and acidified, and the ppt. is extd. with cold dil. soda, pptd. with 25% AcOH and quickly filtered there is obtained (*o*-HO₂CC₆H₄)₂Se₂, m. 294–5°.

CHAS. A. ROUVIER

Fluorene series. III. Derivatives of dibromofluoreneoxalic ester. ADOLF SEIG-LITZ. Univ. Frankfurt a. M. Ber. 53B, 2241–9(1920); cf. C. A. 14, 3666.—From

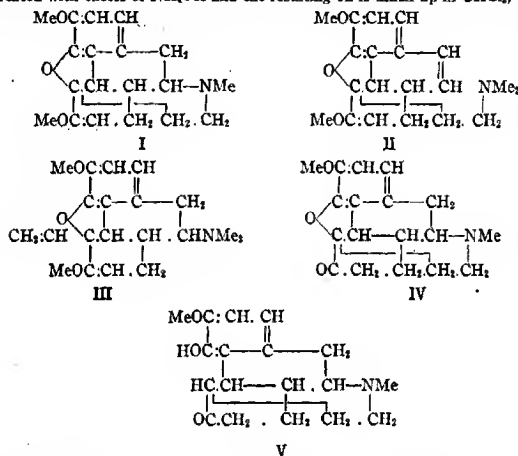
4 g. Et 2,7-dibromofluorene-9-oxalate (A) digested a few min. on the H₂O bath with 20 cc. of 10% KOH, poured into much H₂O, filtered from the 2,7-dibromofluorene (B) and acidified is obtained 1.7 g. of the free acid, slender, orange-yellow needles from AcOH, m. 243° (decompn.), oxidized by cold 30% H₂O₂ in alk. soln. to B, gives an intense brown-green color with FeCl₃ in alc.; phenylhydrazone, fine, lemon-yellow needles from alc., m. 211–2° (decompn.). Methyl ester (C), prepd. like A (12–3 g. from 60 cc. C₆H₆, 8 cc. alc., 1.2 g. Na, 5.9 g. (CO₂Me), and 16.2 g. B), dull yellow needles from AcOH, m. 153–4°; O-benzoyl derivative, from the calcd. amt. of BzCl dropped into a freshly prepd. alc. soln. of the Na compd. of C, canary-yellow needles from AcOH, m. 174–5°; oxime, fine, felted needles from C₆H₆, m. 209–10° (decompn.); phenylhydrazone, faintly yellow needles from alc., m. 188–9° (decompn.). Oxime of A, prisms from alc., m. 226–8° (decompn.); phenylhydrazone, faintly yellow microneedles from alc., m. 182–3° (decompn.). Methyl 2,7-dibromofluorene-9-hydroxyacetate (4–4.5 g. from 5 g. C in 750 cc. Et₂O treated dropwise with 15 g. amalgamated Al filings), needles from ligroin, m. 108°; ethyl ester, rodlets from ligroin, m. 119–20°. With boiling alc. or concd. ac. KOH the HO esters give almost quant. 2,7-dibromodibenzofulvene-9-carboxylic acid (D), bright, deep orange needles from PhMe, m. 263° (decompn.); methyl ester, prepd. by boiling the acid several hrs. with H₂SO₄ in MeOH, yellow needles from AcOH, m. 152–3°; ethyl ester, yellow needles from AcOH, m. 172–3°. 2,7-Dibromofluorene-9-acetic acid, from 8 g. A, 0.37 g. Na and 3 g. BrCH₂CO₂Et by the method described below for E or, in better yield, from D in boiling EtOH-concd. aq. NH₄OH treated to decolorization with Zn dust, long needles and finally thick prisms from C₆H₆, m. 193–4°; methyl ester, from the Me ester of D with amalgamated Al, spears from MeOH, m. 122–3°; ethyl ester, rhombic leaflets from MeOH, m. 94–5°. β-[2,7-Dibromofluorene-9]-propionic acid, from 5 g. A, 0.27 g. Na and 2.5 g. BrCH₂CH₂CO₂Et (yield poor), needles from C₆H₆-ligroin, m. 188–4°. α-Methyl-2,7-dibromofluorene (E), from 5 g. A treated with 0.27 g. Na in 30 cc. alc., boiled with excess of MeI until neutral, then boiled 1.5–2.0 hrs. with 50 cc. of 20% KOH under an air condenser (the alc. distg. off) and poured into cold H₂O, leaves from AcOH, m. 137–8°. α-Ethyl homolog, crystals from MeOH, n. 80–1°. α-Benzyl compound, yellowish leaflets from AcOH, m. 126–7°, more easily obtained in colorless leaflets from the benzal compd. with amalgamated Al in moist Et₂O. The following 2,7-dibromofluorenes were also obtained by reduction of the corresponding fulvenes; α-p-methylbenzyl, rodlets from AcOH, m. 141–2°; α-o-chlorobenzyl, rod needles from AcOH, m. 150°; α-p-methoxybenzyl, silky needles from AcOH, n. 144–5°; α-furfuryl, thick prisms from alc., m. 110–1°; α-phenacyl (from A, Na and 1/2 CH₂Br), long needles from AcOH, m. 183–4°, gives no hydrazone after 10 hrs. boiling with PhNHNH₂; either in alc. or AcOH. The following 2,7-dibromofluorenes were similarly obtained from the Na deriv. of A; α-[naphthyl-1'-methyl], from α-C₁₀H₇CH₂Br, ne, almost colorless needles from AcOH, m. 167–8°; α-[naphthyl-2'-methyl], faintly yellowish rodlets, m. 145–6°. 2,7-Dibromo-9,9'-difluorenyl, from 9-bromofluorene, lit needles from C₆H₆-AcOH, m. 269–70°. 2,2',7,7'-Tetrabromo-9,9'-difluorenyl, from 4 g. A, 0.22 g. Na and 1 g. I, flat leaflets from PhMe-AcOH, m. 317–8° (Schmidt and Wagner, C. A. 6, 1145, give 284°). 2',2'',7'',7''-Tetrabromo-1,4-dibiphenylene-1,3,4-triene (1,2-[2',2'',7'',7''-tetrabromodifluorenylidene-9',9'']-ethane), from 10 g. B and g. Na in 100 cc. alc. heated 3–4 days on a gently boiling H₂O bath with frequent shaking in air, red needles from xylene, does not m. 320°.

CHAS. A. ROULLER

Reduction products of thebaine. MARTIN FREUND AND EDMUND SPEYER with ERNST GUTTMANN. Univ. Frankfurt-Main. Ber. 53B, 2250–64 (1920).—From 10 g. thebaine in 50 cc. H₂O and 33 cc. of N HCl and 2 g. Pt sponge (Loew-Willstätter) shaken with H until no more is absorbed (about 1500 cc. in 50 hrs.), filtered and pptd. with NH₄OH or soda is obtained 5.5 g. crude and 3.3 g. pure dihydrothebaine (I), pris-

matic tables from alc., m. 162-3°, insol. in NaOH. The soda or NH_4OH mother liquors on extrn. with CHCl_3 and evapn. of the CHCl_3 yield 5 g. of a yellow-brown oil showing no tendency to cryst. but giving with alc. picric acid a *picrate*, $\text{C}_{19}\text{H}_{20}\text{O}_4\text{N} \cdot \text{C}_6\text{H}_3(\text{NO}_2)_3\text{OH}$, of I, small columns, blackens 230°, m. 235°; the mother liquors on evapn. give a second viscous *picrate* which on decompn. with NaOH, extrn. with CHCl_3 and evapn. of the CHCl_3 gives a brown-yellow oil yielding with alc. and MeI a *methiodide*, columns from H_2O , m. 244-6°, whose compn. corresponds to $\text{C}_{19}\text{H}_{20}\text{O}_4\text{N} \cdot \text{MeI}$, with 2 MeO groups (Zeisel). *Hydrochloride* of I, from I boiled with NH_4Cl , seps. from H_2O in wart-like crystals, regenerates I with NH_4OH . *Methiodide*, from I digested hot with MeI, needles or columns with $2\text{H}_2\text{O}$, m. 231°, anhydrous prisms from alc.; 15 g. in 50 cc. hot H_2O treated with 50 cc. of 10% NaOH at once forms an oily suspension; after boiling 10 min. and cooling the oil drops change to a semisolid mass which completely solidifies on washing with H_2O and on crystn. from 96% alc. yields quant. *des-N-methylidihydrothebaine* (II or III), quadratic tables, m. 134-5°, easily turned yellow by light, combines with extraordinary ease with MeI in the cold, giving quant. the *methiodide*, felted needles from H_2O , feathery needles from alc., sinters 240°, m. 243°; 14 g. of this boiled 4 hrs. under a reflux with 100 cc. of KOH in AmOH (during which NMe_2 is split off), repeatedly washed with H_2O , shaken with HCl, filtered from the ppt. of unchanged *methiodide* (1-2 g.), sepd. from the HCl layer and concd. to crystn. gives 5 g. of a *phenanthrene compound*, $\text{C}_{17}\text{H}_{16}\text{O}_3$, cubes from AcOH, sinters 149°, m. 150-1°. *Cyanonordihydrothebaine* (I with CN instead of Me on the N), obtained quant. from 1 g. I in 5 cc. CHCl_3 boiled 1 min. with 1 g. BrCN in 5 cc. CHCl_3 , columns from EtOH- CHCl_3 , m. 258-9°. *Dihydrothebaine N-oxide* (I, with $>\text{N}(\text{:O})\text{Me}$ instead of $>\text{NMe}$), a thick, yellow oil, is obtained by heating 1 g. I with 5 cc. of 30% H_2O_2 until it dissolves, decomp. the excess of H_2O_2 with Pt sponge, making alk. and extg. with CHCl_3 ; treated in H_2O with SO_2 and then with NH_4OH , it regenerates I; *picrate*, needles from EtOH- H_2O , m. 209-10°. Small amts. of I heated about 3 min. with a little concd. HCl and then treated with NH_4OH give *dihydrocodeinone* (IV), columns from alc., m. 197-8°; *hydrochloride*, columns from EtOH-Et₂O; *hydriodide*, long needles from H_2O , m. 219-20°; *methiodide*, leaflets, sinters 250°, m. 255°; 13 g. of the *methiodide* in 100 cc. H_2O boiled about 5 min. with 30 cc. of 10% NaOH gives quant. *des-N-methyl-dihydrocodeinone*, $\text{C}_{19}\text{H}_{20}\text{O}_4\text{N}$, prisms from alc., m. 120-1°, whose *methiodide*, rodlets from alc., m. about 280°; attempts to convert this into a N-free substance by means of alkali failed, although NMe_2 was evolved. *Oxime* of IV, white cryst. meal from CHCl_3 decomps. 284°, pptd. from AcOH by NaOH in flocks which redissolve in excess of NaOH but soon sep. again (probably owing to absorption of CO_2 by the NaOH). *Phenylhydrazone*, elongated columns from alc., m. 106-7°. *Norcyanodihydrocodeinone* (1.9 g. from 2 g. IV in 10 cc. CHCl_3 and 1 g. BrCN in 5 cc. CHCl_3 heated on the H_2O bath with stirring until the CHCl_3 is almost all evapd. off), columns from EtOH- CHCl_3 , m. 224-5°, sol. in hot concd. HCl and repptd. by H_2O . *Dihydrocodeinone N-oxide*, from 1 g. IV heated with 5 cc. of 30% H_2O_2 , isolated as the *picrate*, needles from EtOH- H_2O , blackens 228°, m. 231-2° (decompn.). *Dihydrothebainone* (V) (4.5 g. from 5 g. thebaine in 50 cc. of 5% AcOH and 50 cc. colloidal Pd (1 cc. = 0.0025 Pd) shaken with H to satn. (about 2 hrs.), filtered, pptd. with NH_4OH and extd. with CHCl_3), leaflets from alc., sinters 140° m. 150-1°, contains 1 MeO group (Zeisel), sol. in dil. NaOH, repptd. by NH_4Cl ; *hydrochloride*, $\alpha_D - 50.71^\circ$; *hydriodide*, leaflets from EtOH-Et₂O, decomp. 282-3°; *oxime*, from the HCl salt (below) in NaOH and $(\text{NH}_4)_2\text{CO}_3$, needles or columns from alc., m. 253-5°; *oxime hydrochloride*, crystals from H_2O , m. 318°, sol. in concd. HCl, is obtained by boiling V in HCl with NH_4OH , HCl and adding an excess of NH_4OH ; even a NaOH soln. treated with NH_4Cl gives the HCl salt; *methiodide*, obtained quant. from 5 g. V in 50 cc. C_2H_5 allowed to stand 12 hrs. with

somewhat more than 1 mol. MeI, column-like crystals from H_2O , m. around 150° . *Des-N-methyl-dihydrothebaine*, quant. obtained from 5 g. of the above methiodide in 15 cc. hot H_2O treated with stick KOH until a light yellow oil seps., boiled 1 min., cooled, sepd. from the supernatant liquid and pptd. from hot H_2O with CO_2 , columns from 50% alc., m. 183° ; α_D 60.7° (dil. AcOH); *hydriodide*, yellow columns from H_2O , sinters 170° , m. 180° . When 1 g. I in 4 cc. of 2 N AcOH dild. to 25 cc. and 10 cc. of colloidal Pd (1 cc. = 0.0025 g. Pd) previously satd. with H are shaken in H_2 , the absorption is at first very rapid but slows up considerably towards the end (total absorbed 108 cc.; calcd. for 1 mol. H 70 cc.); after filtering, NH_4OH ppts. V from the soln. Likewise, when 1 g. I in 20 cc. hot AmOH is gradually treated with 1 g. Na and shaken with 50 cc. of 2 N AcOH and the AcOH ext. is freed of the last traces of AmOH with Et_2O and treated with excess of NH_4OH and the resulting oil is taken up in $CHCl_3$, there is



obtained 0.6 g. of V.

CHAS. A. ROUILLER

3-Nitrophenazoxine. F. KEHRMANN AND MARIE RAMM. Univ. Lausanne. *Ber.* **53B**, 2285-7 (1920).—From 10 g. $2,4-(O_2N)_2C_6H_3Cl$ and 6 g. $o\text{-H}_2NC_6H_4OH$ in 50 cc. boiling alc. treated in the course of 4 hrs. with 4 g. NaOAc, cooled, filtered, washed with dil. alc. and H_2O , heated almost to boiling in H_2O , dissolved by cautious addition of NaOH, filtered hot, treated with enough solid NaCl so that an abundant sepn. of crystals occurs while still hot and cooled, *2,4-dinitro-2'-hydroxydiphenylamine* is obtained in light brown leaves with metallic luster. The Na salt, mixed with 0.25 its wt. of anhydrous NaOAc, is covered with enough glycerol (dried at 150°), so that it almost all dissolves on shaking and warming and is then slowly heated to 200° until a portion gives with alc. KOH a violet color without a brownish tinge; it is then hoiled up with H_2O , filtered, dried and extd. with C_6H_6 and the crystals which sep. from the C_6H_6 ext. when it is sufficiently concd. are repeatedly crystd. from alc. There is thus obtained a few % of *3-nitrophenazoxine* as dark brown needles with a brass luster, darkens about 200° (decompn.), does not m. 300° , slightly sol. in C_6H_6 and Et_2O with yellow color and vivid yellowish green fluorescence, more easily in alc. with orange-red and in $CHCl_3$ with golden yellow color (the last 2 solns. do not fluoresce markedly),

in concd. H_2SO_4 with red-brown, in alc. alkalis with pure violet color; *acetyl derivative*, reddish yellow tablets from C_9H_6 , m. 135.5° . The NO_2 compd. heated with SnCl_2 , HCl and a little Sn in enough alc. gives a colorless soln., which, on removal of the alc., deposits a Sn double salt of 3-aminophenazoxine in leaves or needles, which, after removal, of the Sn in H_2O with H_2S , gives on oxidation with FeCl_3 at room temp. and salting out with NaCl 3-aminophenazoxonium chloride (*Ann.* 414, 157(1917)). C. A. R.

NOYES, W. A.: *Organic Chemistry for the Laboratory*. 4th Ed. revized. Easton, Pa.: The Chemical Publishing Co. 293 pp. \$3.50.

Borneol. H. YUWAMURA. Japan 36,285, Apr. 28, 1920. Sodium amalgam, prepd. from 46 g. Na and 1435 g. Hg , is mixed with 100 g. camphor, made into a paste with alc. and steam-distd. Almost pure borneol results.

II—BIOLOGICAL CHEMISTRY

HATTIE L. HEFT, EDGAR G. MILLER, JR., AND WILLIAM J. GIES
A—GENERAL

FRANK P. UNDERHILL

Amylase of *Rhizopus tritici*, with a consideration of its secretion and action. I. L. HARTER. Bur. Plant Ind. *J. Agr. Res.* 20, 761-86(1921).—Powdered mycelium was largely used in the expts. although exts. of the mycelium were used for certain phases of the work. The powdered mycelium was prepd. by acetone treatment. The fungus was grown on a modified Czapek's nutrient soln. or on sweet potato bouillon at $25-35^\circ$. The substitution of NH_4NO_3 for NaNO_3 in the nutrient soln. influenced the growth of the fungus. Irish potato or sweet potato starch was used directly or for the prepn of starch paste. Two cc. of toluene were added to each flask and the hydrolyses were carried out at different temps. The enzyme was inactivated by steaming in a sterilizer for 15 mins. The soln. was then filtered through cotton and the reducing sugars were detd. The intermediate starch products were not estd. An active amylase was found, of which some was retained in the mycelium and a portion diffused into the substratum. The enzyme acts on raw sweet potato starch and on Irish potato starch, but less energetically than on s'arch paste. The dried mycelium may be held for months at temps. of from 9 to 35° without much deterioration, but at 60° it gradually weakens and is destroyed in 100 hrs. 45° is the optimum temp. for digestion of starch. If glucose is added to a system the hydrolysis of starch paste is retarded, the amt. having no influence on the results. With a const. amt. of enzyme powder the total amt. of reducing sugars formed in a soln. of starch paste increases with the increase of vol. of the soln. up to a certain point and then decreases. Unless the equil. of the system is disturbed by changing the temp. and dilg. the soln. no end-point in the hydrolysis of starch is reached. If judged by the I test an end-point is obtained, but a quant. detn. of reducing sugars does not account for all the starch. The temp. at which the fungus is grown has a marked influence on the production of intercellular amylase. Enzyme powder prepd. from mycelium grown at 9° hydrolyzed about 4 times as much starch as powder from mycelium grown at 40° . Powder from mycelium grown at 29° was intermediate. The results of this investigation show a "quant. regulation" of the enzyme. The hydrolyzing power of the mycelium was greater when starch than when glucose or glucose plus starch was used in the medium. If grown on sweet potato bouillon containing both starch and sugars a unit wt. of the mycelium will hydrolyze more starch than when grown on any other combination. The vigor of growth of the fungus was correlated with the hydrolytic power of the powdered enzyme prepn. The results appear to indicate that it is not so much the source of the carbohydrate which influences the quant. production of the enzyme as it is the influence which it has on the growth of the fungus, on which the secretion of the enzyme depends. The enzyme powder from a young

mycelium was more active than a prepn. from an old mycelium. *Rhizopus tritici* is responsible for large losses of sweet potatoes and other vegetables in storage and transit.

F. C. COOK

The scientific work of Armand Jorissen. F. SCHOORS AND R. VIVARIO. *J. Pharm. Belg.* 3, 121-7, 137-42, 153-7(1921).—A review of the scientific work of Armand Jorissen, member of the Faculty of Medicine of the University of Liège, including a bibliography of his publications.

A. G. DUMÉZ

Review of recent work on enzyme action. R. J. S. McDOWALL. *Sci. Progress* 15, 406-34(1921).—Comprehensive review with sections devoted to the various physicochem. factors which influence the velocity of enzyme action, to the various groups of enzymes, to adjuvans (co-enzymes), and to antagonists (anti-enzymes). J. S. H.

Studies in the mechanism of enzyme action. I. Role of the reaction of the medium in fixing the optimum temperature of an enzyme. ARTHUR COMPTON. *Proc. Roy. Soc. London (B)* 92, 1-6(1921).—From expts. made with the maltase of *Aspergillus oryzae*, the conclusion is drawn that the optimum temp. for any enzyme is independent of the concn. of the enzyme, provided that the duration of the action and the chem. reaction (H-ion concn.) of the medium remain const. JOSEPH S. HEPBURN

The principle of Carnot and the physicochemical evolution of the living organism. CH.-EUG. GUYE. *Arch. sci. phys. nat.* [5] 2, 176-213(1920).—The discussion is largely philosophical and metaphysical. The conclusion is drawn that, while the principle of Carnot governs physicochem. evolution including "statistical actions," the cause of the origin and the organization of life and of thought must be sought in the actions of individuals.

JOSEPH S. HEPBURN

Formation of the nucleolus in the life of the animal cell. J. BRONTÉ GATENBY. Univ. London. *Sci. Progress* 15, 480-2(1921).—The nucleolus is a sep. and very important nuclear element, whose functions in the metabolism of the cell are of signal importance. It may produce yolk proteins in the egg cell, and fat in the somatic cell, and, in certain species, may cause the formation of secondary nuclei independently of the chromosomes.

JOSEPH S. HEPBURN

Contractile vacuoles. HENRY H. DIXON. Trinity Coll., Dublin. *Nature* 106, 343(1920).—A contractile vacuole is not an organ of a cell, but results from the local accumulation of any sol. substance. Only cells which lack a continuous cell wall contain such vacuoles. The accumulated crystalloid, by virtue of its osmotic pressure, pushes back the protoplasm of the cell, and forms a cavity, which enlarges as water enters it. The vacuole continues to enlarge, until but a very thin film of protoplasm separates its contents from the water which surrounds the cell. Finally this film breaks as a result of further expansion of the vacuole; and the contents of the latter mingle with the surrounding water. The elasticity of the protoplasm now drives the walls of the cavity together, heals the rupture and obliterates the vacuole. However, the viscosity of the protoplasm leads to a delay in recovery, and causes the appearance of the radiating canals. If a cell acquires a complete cell wall, the protoplasmic film has sufficient support, and the vacuoles become permanent. JOSEPH S. HEPBURN

The question of fat-formation from carbohydrate in man. GERTRUD BAUMGART AND MARIA STEUBER. Berlin. *Deut. Arch. klin. Med.* 134, 141-7(1920).—It is shown by indirect calorimetry that fat is formed in man from carbohydrates.

JULIAN H. LEWIS

The production of intracellular acidity by neutral and alkaline solutions containing carbon-dioxide. M. H. JACOBS. Univ. Penn. *Am. J. Physiol.* 53, 457-63(1920).—By using cells from the flowers of *Symphytum peregrinum* which contain a natural indicator sensitive to CO₂ J. has shown that the cells are very permeable to CO₂. A condition of intracellular acidity can be produced by a slightly alk. soln. of CO₂ in 0.5 M NaHCO₃ almost as effectively as by a soln. of CO₂ in H₂O, though the *p_H* of the latter is approx. 4000 times as great as that of the former.

J. F. LYMAN

The direct synthesis of urea by urease. H. P. BARENDRECHT. Delft. *Recl. trav. chim.* 39, 603-5(1920).—Mattaar (*C. A.* 15, 67) described fruitless attempts to demonstrate by the xanthidrol reaction (Fosse, *C. A.* 11, 160) the presence of urea in a mixt. of urease and $(\text{NH}_4)_2\text{CO}_3$ and concluded that B.'s reported synthesis (*C. A.* 14, 749) was not true. B. replies by explaining that a synthesis was not to be expected under the conditions used by M. According to B.'s radiation hypothesis the other proteolytic enzymes are also present further to convert the urea synthesized. Consequently the disappearance of NH_4 under the influence of urease constitutes proof that urea was synthesized intermediately.

B. J. WITZEMANN

The direct synthesis of urea by urease. TH. J. F. MATTAAR. Univ. Leyden. *Rec. trav. chim.* 40, 65-6(1921).—M. replies to B. (cf. preceding abstr.) without describing any new expts. and rejects B.'s expts. as evidence of synthesis. H. P. BARENDRECHT, 40, *Ibid* 66, closes the discussion.

E. J. WITZEMANN

The solubility, rate of absorption and of evolution of gases, as influenced by colloids, with special reference to physiology (KING) 2. Chemistry of diastase (YAMAZAKI) 10.

FARR, CLIFFORD BAILEY: Outlines of Internal Medicine for the Use of Nurses and Junior Medical Students. Third Ed. Philadelphia and New York: Lea & Febiger. 406 pp. For review see *Am. J. Med. Sci.* 161, 280(1921).

B—METHODS AND APPARATUS

STANLEY R. BENEDICT

A method for the determination of chlorine in solid tissues. RICHARD D. BELL AND EDWARD A. DOISY. Walter Reed Gen. Hosp. and Harvard Med. School. *J. Biol. Chem.* 45, 427-35(1921).—The material is oxidized with H_2SO_4 and $\text{K}_2\text{S}_2\text{O}_8$, or $(\text{NH}_4)_2\text{S}_2\text{O}_8$, in an apparatus of form shown in sketch. The first absorption tube contains 2 g. Na_2CO_3 for every g. of tissue and the second contains 1 g. (in all). Each contains 10 cc. H_2O and a few drops caprylic alcohol. The finely ground tissue is weighed into the digestion tube, a minute drop of Hg and 2-3 pieces of broken quartz are added. After setting up apparatus and starting current of air, 2 cc. of H_2SO_4 per g. of tissue are added and the mixt. is heated slowly until the larger pieces of tissue have dissolved. After boiling for 5 min., the tube is allowed to cool somewhat, 2 g. $\text{K}_2\text{S}_2\text{O}_8$ and a fresh piece of quartz are added and the heating is resumed. If the mixt. is not clear in a few min., more $\text{K}_2\text{S}_2\text{O}_8$ is added in the same way. When clear, the air current is stopped and all connecting and absorption tubes are washed into a 150-cc. Erlenmeyer flask, some quartz and Me orange are added and then 30% H_2SO_4 until slightly acid.

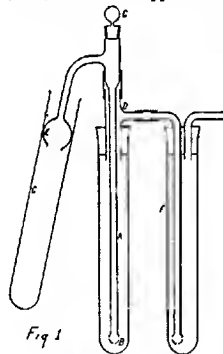


Fig. 1

Boil for a few min., keeping slightly acid, then add 5 cc. of soln. containing 5.812 g. AgNO_3 and 250 cc. concd. HNO_3 per liter, evap. to 15 cc. and dil. to 25 cc. in volumetric flask. Centrifuge and titrate Ag in clear liquid by method of McLean and Van Slyke (*C. A.* 9, 1588).

I. GREENWALD

The estimations of bile acids in bile. CARL L. A. SCHMIDT AND A. E. DART. Univ. Calif. *J. Biol. Chem.* 45, 415-21(1921).—To 10 cc. of hile (more if dil.) add 85 cc. EtOH , heat almost to boiling, filter and wash with EtOH until the vol. of the cooled filtrate is 100-cc. Evap. two 20-cc. portions in evap. dishes and the remainder in a Ni crucible. This portion is oxidized by fusion with Na_2CO_3 and Na_2O_2 and total S is detd. in the usual manner. The residue from one of the 20 cc. portions is dissolved in H_2O , dild. to 10 cc. and 2-cc. portions are used for detn. of $\text{NH}_4\text{-N}$ (*C. A.* 5, 509, 2586).

The other is dild. to 10 cc. with 8% NaOH and heated at 100° for 6-8 hrs. $\text{NH}_4\text{-N}$ is then detd. in 2-cc. portions. The difference between $\text{NH}_4\text{-N}$ of hydrolyzed and unhydrolyzed bile represents the taurine and glycine N of the bile acids. The taurine N is calcd. from the total S, there being no appreciable quantities of other S compds. The difference between total $\text{NH}_4\text{-N}$ due to bile acids and that due to taurine is 103% of the glycine N, glycine giving abnormally high values for $\text{NH}_4\text{-N}$. The values obtained were, per 10 cc. of bile, ox, 7.1 and 11.8 mg. taurine N, 10.2 and 5.2 mg. glycine N; pig, 3.9, 3.2 and 4.0 mg. taurine N, 14.1, 16.4 and 12.0 mg. glycine N; sheep, 18.1 and 20.4 mg. taurine N, no glycine; dog, 2.1 and 2.1 mg. taurine N, no glycine; human, 0.8, 0.6 and 0.7 mg. taurine N, 0.8, 0.6 and 0.8 mg. glycine N. In a specimen obtained at autopsy, these values were 2.9 and 4.7 mg., resp.

I. GREENWALD

A system of blood analysis. Supplement II. Simplified method for the determination of chlorides in blood or plasma. J. C. WHITEHORN. Harvard Med. School. *J. Biol. Chem.* 45, 449-60(1921).—The tungstic acid filtrate obtained in the system of blood analysis of Folin and Wu (*C. A.* 13, 2541) is used. To 10 cc. in a porcelain dish add 5 cc. $M/35.46$ AgNO_3 , stir thoroughly, add 5 cc. concd. HNO_3 , mix, let stand 5 min., add 0.3 g. $\text{FeNH}_4(\text{SO}_4)_2$, and titrate excess of Ag with $M/35.46$ KCNS or $(\text{NH}_4)_2\text{CNS}$ to a definite salmon-red, which persists for at least 15 seconds. The difference between 5 and the no. of cc. of KCNS required = mg. Cl per cc. of blood or plasma. Na_2WO_4 is generally free from Cl. It may be tested by mixing 1 vol. 10% Na_2WO_4 with 2 vols. concd. HNO_3 and testing the filtrate with AgNO_3 . If Cl is found, the Na_2WO_4 may be purified by adding an equal vol. of EtOH to a cooled 50% soln. and filtering after 10 min. The large amt. of HNO_3 is needed to agglutinate the AgCl in large clumps, offering little surface. The method is accurate to within 1.5%, as compared with von Koranyi's or with that of Bell and Doisy (2nd preceding abstract).

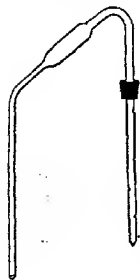
I. GREENWALD

The determination of chlorides in blood plasma. J. HAROLD AUSTIN AND DONALD D. VAN SLYKE. Rockefeller Inst. *J. Biol. Chem.* 45, 461-3(1921).—Some specimens of plasma give high values for Cl by the method of Van Slyke and Donleavy (*C. A.* 13, 2050). The method of Austin and Van Slyke (*C. A.* 14, 2354) in which the Cl is pptd. in the protein-free filtrate is, therefore, preferable for plasma as for whole blood.

I. GREENWALD

The removal of ammonia from urine preparatory to the determination of urea. GUY E. YOUNGBURG. Univ. Buffalo. *J. Biol. Chem.* 45, 391-4(1921).—The detn. of NH_3 as part of the detn. of urea is eliminated by treatment of the urine with permutite before addition of the urease. Place 3-4 g. dry permutite in a 200-250 cc. flask, add 20-25 cc. of a 1:10 or 1:5 dila. of urine with H_2O , agitate for 5 min., allow to settle and decant or filter. To 5 cc. of liquid add 2 cc. of urease soln. (Folin and Youngburg, *C. A.* 13, 2052) and 2 drops of soln. containing 142 g. Na_2HPO_4 and 120 g. NaH_2PO_4 per liter. After 15 min., complete the detn. as described by Van Slyke and Cullen (*C. A.* 8, 2406).

I. GREENWALD



An improved apparatus for use in Folin and Wu's method for the estimation of urea in blood. THOMAS WATSON AND H. L. WHITE. Univ. Southern Calif. *J. Biol. Chem.* 45, 465-6(1921).—A tube of the form shown is used to break up the foam during the distn. It may be used also in Kjeldahl distns.

I. GREENWALD

The determination of chlorides in trichloroacetic acid filtrates from whole blood and plasma. MILLARD SMITH. Harvard Med. School. *J. Biol. Chem.* 45, 437-47(1921).—The method of Van Slyke and Donleavy (*C. A.* 13, 2050) gives results that are too high, as are also those obtained with tungstic acid filtrates. The methods of Foster (*C. A.* 11, 3290) and of Austin and Van Slyke (*C. A.* 14, 2354) are sometimes troublesome because of failure of the AgCl to separate properly. S. ppts. the protein with CCl_4 .

COOH and titrates Cl by a modification of the technic of McLean and Van Slyke (*C. A.* 9, 2259). The addition of H_3PO_4 improves the end-point. Solns. of pure CCl_3COOH give good pptns. of AgCl , but those of the U. S. P. grade do not. However, if the pptn. be made in the presence of 10% EtOH, the AgCl separates well. To 40 cc. H_2O , or 14% EtOH, add 5 cc. plasma or blood and rinse out the pipet with the liquid. Add 5 cc. 20% CCl_3COOH , stopper and shake at intervals for 10-15 min. Filter through Cl-free paper, measure 10 cc. filtrate into centrifuge tube, add 2 cc. AgNO_3 soln. (11.624 g. AgNO_3 , 300 cc. HNO_3 [d. 1.42] dild. to 1 liter), shake vigorously and centrifuge. Pipet off 10 cc., add huffer soln. and 1 cc. starch soln. (prepared by boiling 5 g. starch in 400 cc. H_2O for 5 hrs., dilg. to 1 liter and filtering through cotton) and titrate to permanent blue with KI soln. The huffer soln. is prepd. by dissolving 446 g. cryst. Na_2 citrate and 50 cc. 80% H_3PO_4 in 800 cc. hot H_2O and, when cool, adding a soln. of 20 g. NaNO_2 in 100 cc. H_2O and dilg. to 1 liter. The optimum amt. required should be found by a series of detns. in which an 0.85-0.9% NaCl soln. is used instead of blood. It will generally be about 2.5 cc. After this optimum has been detd., the KI soln. is dild. so that 8.0x — cc. KI = g. NaCl per liter of blood (x = vol. of KI required to give end-point with buffer soln. and starch). A sample yielding 583 mg. NaCl per 100 cc. by von Koranyi's method (*Z. klin. Med.* 33, 1(1897)) gave values from 579 to 585, av. 583 mg., in a series of 9 detns. by this method. Cf. Bell and Daisy, above.

I. GREENWALD

A simple device for measuring rate of metabolism. HARRY M. JONES. Univ. Ill. Coll. of Medicine. *Arch. Intern. Med.* 27, 48-60(1921).—A portable apparatus by means of which the time required for the subject to consume 1 liter of O_2 is measured.

I. GREENWALD

The effect of certain blood constituents on picrate solutions. S. R. BENEDICT AND EMIL OSTERBERG. *Arch. Intern. Med.* 27, 135-6(1921).—The claim of Cowie and Parsons (*C. A.* 14, 3684) as to the effect of AcMe and epinephrine added to blood upon the blood sugar detn. is denied. The former exerts no appreciable influence in concns. less than 7 mg. per 100 cc. blood. Above that, its effect increases until at about 20 mg. it is somewhat more than that of an equal amt. of glucose. Epinephrine produces an effect equivalent to that of twice its wt. of glucose.

I. GREENWALD

The determination of acetone and aldehyde in the same fluid. W. STEFF AND W. ENGLHARDY. *Biochem. Z.* 111, 8-16(1920).—In the detn. of acetone and aldehyde present in the same soln. there are difficulties which inhibit the measurement of the one when the best method for the detn. of the other is utilized: the iodoform method, which is quant. for acetone, gives too low results for aldehyde, while the detn. of aldehyde by Ripper's method (*Sitzber. akad. Wissenschaft. Abt.* 26, 108-109, 844(1899-1900)) in its usual form does not suffice for acetone. The method for aldehyde of Fürth and Charnass (*C. A.* 5, 51) is inexact when compared with Ripper's method. In fact, the iodoform method for the detn. of the 2 compds. in their mixts. is worthless. The only method yielding exact results is that of Ripper, modified by extending the reaction time to 40 hrs.

F. S. HAMMETT

Influence of ammonium carbonate in urine on certain tests. CLIFFORD MITCHELL. *Hahnemannian Monthly* 56, 152-5(1921).—When alkali carbonates, including $(\text{NH}_4)_2\text{CO}_3$, are present in the urine, they decrease the titratable acidity of that secretion as detd. with phenolphthalein as the indicator. They also give rise to fallacious (usually high) results in the volumetric detn. of phosphates with $\text{UO}_2(\text{NO}_3)_2$, using the ferrocyanide indicator. In clinical diagnosis, the acidity of a urine must be interpreted in connection with its odor and sp. gr. and the character of its sediment.

JOSEPH S. HEPBURN

Determination of glucose in the presence of lactose. E. HILDR. *Faculté méd., Paris. Ann. chim. anal. chim. appl.* [2], 2, 78-80(1920).—Pathological urines may contain both glucose and lactose. Both sugars may be detd. by detn. of the reducing power both before and after hydrolysis of the lactose to glucose plus galactose; to

produce this hydrolysis, use is made of a catalyst, which is prepd. by soln. of 180 g. Na benzenesulfonate (free from Fe) and 49 g. abs. H_2SO_4 in sufficient water to make 1 l. The procedure is briefly: 100 cc. of urine are clarified by addition of 10 cc. of Courtonne's soln. of neutral Pb acetate, and the approx. reducing-sugar content of the resulting soln. is detd. by titration. A vol. of the soln. containing not more than 1 g. of sugar is placed in a 100-cc. graduated flask with 20 cc. of the catalyst soln. and sufficient distd. water to fill the flask to the mark. The contents of the flask are mixed and filtered. A portion of the filtrate is used for the direct titration of the reducing sugar with Fehling soln., which has been dild. with 4 vols. of water plus 5 or 6 drops of concd. NaOH soln. Another portion (50 cc.) of the filtrate is placed in a graduated flask of 50 cc. capacity, which is then kept for a period of 6 hrs. in a thermostat at a temp. of 95° to 98° ; it is cooled, the contents are restored to a vol. of 50 cc. if necessary, and are mixed; their reducing-sugar content is then detd. by titration with Fehling soln. in the manner just outlined. In each titration 10 cc. of the mixed Fehling soln. are used. If n be the number of cc. of the filtrate required to reduce the Fehling soln. completely prior to inversion, and n' be the number of cc. of the filtrate required to reduce the Fehling soln. completely after inversion, and if X represent the wt. in g. of hydrated lactose and y represent the wt. in g. of anhydrous glucose contained in 100 cc. of the filtrate, then $X = (3.55/n') - (3.55/n)$ and $y = (1.458/n') + (3.34/n)$. From the concn. of each of the 2 sugars in the filtrate, it can readily be calcd. for the original urine.

JOSEPH S. HEPBURN

Estimation of pepsin in urine. S. NOMURA. *Chuo Igakkai Zasshi* No. 273, 1136-42(1918); *Jap. Med. Literature* 5, 30(1920).—In order to det. pepsin in the urine, the phosphates must be pptd. without making the urine too alk. Normally sufficient pepsin to digest the protein contained in 4 cc. of a 1% casein soln. is present in 15 to 25 cc. of urine. An abnormal pepsin content of the gastric juice gives rise to an abnormal concn. of that enzyme in the urine.

JOSEPH S. HEPBURN

Fractional examination of the gastric contents. ROY UPHAM. *J. Am. Inst. Homeopathy* 13, 622-6(1921).—The fractional examn. of gastric contents is far superior to any other method thus far devised. Duodenal ulcer causes a characteristic curve in the acidity of the gastric contents (detd. by the fractional method); and the rise during the first hour is far in advance of the normal. Cases with a sustained acidity, or with a rising acidity during the second hour, are due to an irritated condition of the stomach, caused by either gastric ulcer, or chronic appendicitis, or colitis, or gall-bladder conditions. These gall-bladder conditions give rise to a curve characterized by a marked delay in the onset of digestion in the first hour and a further delay in the second hour, with a rise of acidities in advance of those encountered in the first hour. Achylia gastrica shows a characteristic diagnostic curve with a lack of spread between the total acidity and the free HCl. Carcinoma has a characteristic curve with an increased spread between the free HCl and the total acidity, due to org. acids produced by fermentation.

JOSEPH S. HEPBURN

Rapid determination of sulfur in the urine. CH. RABAUT AND A. STILLMUNKÉS. *Faculté med., Toulouse. Progrès médical* 1920, 50-1; *Repert. pharm.* (3), 33, 37-8 (1921).—The methods described depend on the pptn. of the SO_4 ion by means of a soln. of $BaCl_2$ in 5% HCl; this soln. is adjusted so that 1 cc. equals 1 mg. SO_4 . The pptn. is made in centrifuge tubes of 20 cc. capacity. *Detn. of S present as preformed sulfate.*—10 cc. of urine are placed in the centrifuge tube; 0.2 cc. of the $BaCl_2$ soln. is added; and the pptd. $BaSO_4$ is made to settle by centrifugation for 2 to 3 min. A new, measured vol. of the $BaCl_2$ soln. is now added, and an additional ppt. of $BaSO_4$ forms and is deposited by centrifugation; this procedure is repeated until a ppt. no longer forms on addition of the $BaCl_2$ soln. From the vol. of $BaCl_2$ soln. used for complete pptn. of the SO_4 ion, the preformed sulfate content of the urine is calcd. In the presence of the HCl, only the SO_4 ion is pptd. by the Ba ion; conjugate sulfates are not saponified

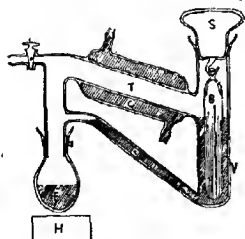
since the reaction occurs at room temp. *Detn. of total S.*—After incineration of the urine in the usual manner, a clear soln. is obtained, in which the total S is then detd. by pptn. as BaSO_4 in the manner just described. *Detn. of total sulfate—performed plus conjugate.*—From 50 to 100 cc. of urine are mixed with one-tenth their vol. of pure HCl , and are heated for 1 hr. in a flask beneath a reflux condenser. The liquid becomes more or less dark in color; it is filtered, if necessary, after cooling; the ppt. is washed; and the SO_4 ion is detd. in a 10-cc. aliquot of the combined filtrate and washings by pptn. as BaSO_4 in the manner described above. These methods are exact and rapid, and may be applied to all samples; it is not necessary to decolorize pigmented samples by means of KMnO_4 , a procedure that may liberate elementary Cl , which then decomposes a portion of the neutral S compds. and thereby changes the partition of the S.

JOSEPH S. HEPBURN

Determination of coagulable protein in serum. W. N. BERG. Bur. Animal Ind. *J. Lab. Clin. Med.* 6, 223-6(1921).—One-half cc. serum is pipetted accurately from a pipet graduated to 0.01 cc. into a clean, weighed bacteriol. test-tube and 9 cc. distd. water are added. The tube is warmed and 0.02 *N* HOAc added, 0.2-0.3 cc. at a time. It is heated, but not boiled, with each addition. When the protein flocculates the tube is heated almost to boiling and allowed to stand 5 min. When pptn. is maximal the supernatant liquid is clear. If any opalescence persists, 0.1-0.2 cc. 0.02 *N* HOAc is added and the liquid again heated. The tube is centrifuged 20 min. at 2400 revolutions and the supernatant liquid poured off completely. The tube is dried *in vacuo* over H_2SO_4 and weighed. Triplicates varied within a fraction of a mg. Coagulable protein averaged 91.4% of the total solids-not-ash.

R. R. LONG

An apparatus for continuous dialysis or extraction. HUBERT MANN. Montefiore Hosp., N. Y. *J. Biol. Chem.* 44, 207-9(1920).—The app. is operated at reduced pressure and is especially suitable for the extn. of labile substances which are destroyed either by oxidation or high temp. A small amt. of solvent can be used for the extn. of a large amt. of material and the extd. substances are at the same time concd. By using a collodion bag or other dialyzing membrane the diffusible substances in plant and animal tissues can be extd. and concd., e. g., amino acids from blood and muscarin and other thermolabile alkaloids from fungi. The method of operation is as follows: Place the substance to be extd. or dialyzed in the bag, *B*, (which may be of cotton, collodion or other material), and suspend the bag in the vessel *V* fitted with a ground stopper, *S*, provided with a Hg cup. Introduce into the vessel *V* enough solvent to overflow through the tube *t* into the flask *F* partly filling the flask. Exhaust the app. to the desired degree through the tube fitted with the stopcock *s* which should then be closed. Allow H_2O to circulate through the condenser *C* and warm the flask *F* by the heating unit *H* (an incandescent bulb may be used). Continuous evapn. of the fluid in the flask *F* and condensation of this



evapd. fluid in the condenser tube *T* occurs. The vessel *V* continuously receives a supply of freshly distd. solvent and discharges its previous content into the flask *F* in which continuous evapn. and concn. of non-volatile matter take place. When H_2O is used as the solvent and the app. is well exhausted, the flask need not be warmed more than 10-15° above room temp.

A. P. LOTHROP

The determination of sodium in blood. EDWARD A. DOISY AND RICHARD D. BELL. Wash. Univ. School of Med. and Harvard Med. School. *J. Biol. Chem.* 45, 313-23 (1921).—The Na is pptd. as the complex Na Cs Bi nitride described by Ball (*C. A.* 5, 44). The method is almost as accurate as the older procedures but requires much less

material and time. As small an amt. as 0.01 mg. of Na yields a ppt. in a final vol. of 2 cc. None of the ions commonly occurring with Na interferes with the pptn. *Reagents.* *Bi Cs nitrite soln.*—Dissolve 30 g. of Na-free KNO_3 in about 60 cc. of pure H_2O and add a soln. containing 3 g. of $\text{Bi}(\text{NO}_3)_3$ (a stock soln. containing 60% of the cryst. salt in 2 *N* HNO_3 is convenient). If a ppt. forms add dil. HNO_3 carefully until it redissolves. Add a strong soln. containing 1.6 g. of CsNO_3 and 1 cc. of 2 *N* HNO_3 . Dil. the soln. to 100 cc. and remove any turbidity with dil. HNO_3 . The reagent should be a clear orange color. Allow to stand for 24 hrs. and filter if necessary. Keep under illuminating gas in a cold room (1°). Pure KNO_3 may be made by passing nitrous fumes into a 25% soln. of Merck's or Eastman's Na-free K_2CO_3 . Drop HNO_3 (sp. gr. 1.2) from a separatory funnel into a flask containing As_2O_3 and pass the fumes into the carbonate soln. The reaction is complete when the soln. gives off many fine bubbles of CO_2 on shaking. *Acetone:* redistd. and kept ready for use at 1° ; a 50% soln. of acetone satd. at 1° with NaCsBi nitrite. *For volumetric procedure:* 0.1 *N* or 0.05 *N* KMnO_4 , 0.1 or 0.05 *N* $\text{H}_2\text{C}_2\text{O}_4$ concd. H_2SO_4 dild. with an equal vol. of H_2O . *Method of Analysis.*—Transfer 1 cc. of urine to a pointed Pyrex tube (after a tube has been rendered unserviceable by H_3PO_4 in non-protein N detns., heat it in an O-gas flame and draw out to a point; tubes with small tips and thin walls stand heating best and the pointed tips provide a const. stream of bubbles so that no boiling stones are necessary). Add a few drops of concd. H_2SO_4 and 5 cc. of concd. HNO_3 and keep the liquid boiling gently with a low flame until it is colorless; urine requires about 10 min. With blood or plasma much time can be saved by pptg. the proteins with $\text{CCl}_3\text{CO}_2\text{H}$. Transfer 5 cc. of whole blood or plasma to a 50-cc. volumetric flask containing 35 cc. of H_2O and add 5 cc. of 20% $\text{CCl}_3\text{CO}_2\text{H}$. Dil. to the mark, mix and allow to stand for 30 min. Filter through a dry paper. Pipet 10 cc. of the filtrate (equiv. to 1 cc. of blood) into a 50-cc. Erlenmeyer flask fitted with a trap (a convenient trap can be made by blowing a bulb on the closed end of a soft glass test-tube a hole is then blown in the side of the bulb, which is then cut off from the tube) to prevent loss by bumping, and add 1 drop of concd. HNO_3 . Heat on a piece of asbestos on a hot-plate until brown fumes from the acid are evolved. Cool and wash off the trap with a few drops of H_2O . Cool the soln. to 10 – 12° and add 3 cc. of reagent for each mg. of Na expected. Stopper the flask with a 2-bored rubber stopper bearing 2 short glass tubes bent at right angles. Fit one with a short rubber tube with glass plug and the other with a Bunsen valve and plug. Pass illuminating gas free from H_2S into the flask for a few secs. and replace the plugs. Put the flask into a cold room at 1° and keep there for 24 hrs. Filter rapidly on a Gooch crucible and wash quickly with ice-cold 50% acetone satd. with Na Cs Bi nitrite. 10 cc. is used for the washing; blow 2 cc. from a miniature wash bottle (made from a 10-cc. graduated cylinder) into the pptn. flask. Stop the suction and pour the liquid on to the mat; repeat 4 times. Use 10 cc. of pure acetone to complete the transfer of the ppt. to the Gooch crucible. Place the Gooch crucible and contents in a tall 200 cc. beaker and add at least twice the amt. of standard KMnO_4 soln. necessary for oxidation together with enough H_2O to cover the crucible. Stir the ppt. loose from the crucible and asbestos. Pour in 10 cc. of 1:1 H_2SO_4 while stirring the liquid. After a few min., heat to 75° , add an excess of standard $\text{H}_2\text{C}_2\text{O}_4$ and finish the titration with KMnO_4 . Run a blank on the reagents under similar conditions. $\text{Cc. KMnO}_4 \times \text{normal factor} \times 8 = \text{mg. O used}$; $\text{mg. O used} \times 7.82 = \text{mg. ppt.}$; $\text{mg. ppt.} \times 0.03675 = \text{mg. Na}$. Gravimetric and colorimetric methods are also described, but the volumetric procedure outlined above is preferred on account of its greater speed and accuracy. The av. amt. of Na in beef blood is 275 mg. per 100 cc. and in swine blood 214 mg. The amt. is const. in the blood of the same species, the max. variation found being only 7%. A. P. L.

The iodometric determination of copper and its use in sugar analysis. I. *Equilibria in the reaction between copper sulfate and potassium iodide.* P. A. SHAFFER.

AND A. F. HARTMANN. Wash. Univ. Med. School. *J. Biol. Chem.* **45**, 349-64(1921). —"Both cupric and cuprous salts may be detd. iodometrically by means of the reversible reaction $\text{Cu}^{++} + \text{I}^- \rightleftharpoons \text{Cu}^+ + \text{I}_2$. The position of equil. has been detd. for the reaction, $\text{CuSO}_4 + N \text{KI} = \text{CuI} + \text{I}_2 + \text{K}_2\text{SO}_4$, at ratios of from 1 to 10 KI: 1CuSO_4 at various dilns. For the detn. of cupric salts KI must be added to give a final concn. of about 0.25 M (4-5 g. per 100 cc. of soln.). For the detn. of cuprous salts the soln. must be so dild. that the final concn. of Cu and of KI does not exceed about 5 millimolar each. The conditions found empirically by Gooch and Heath (*C. A.* **1**, 2992) for cupric salts and by Maclean (*C. A.* **10**, 1873; **13**, 2889) and Scales (*C. A.* **10**, 579) for cuprous salts comply with these requirements." II. Methods for the determination of reducing sugars in blood, urine, milk, and other solutions. *Ibid* 365-90. —The reversible reaction, $\text{Cu}^{++} + \text{I}^- \rightleftharpoons \text{Cu}^+ + \text{I}_2$, may be caused to go to completion in either direction so that either the cupric or cuprous Cu in a mixt. of the two forms may be detd. by iodometric titration. Detailed methods are given for both cupric and cuprous titrations, but the latter is generally preferred; large amts. of KI are needed for the cupric titration and the end-point is less easily seen and less permanent. As the original must be consulted for the charts and tables for the conversion of Cu into terms of sugar, the details of the methods can also be obtained there. In the opinion of S. and H., "both methods are preferable on the grounds of convenience, speed, and reliability to any other volumetric or colorimetric procedures for the detn. of reducing sugar."

A. P. LOTHROP

The determination of acetone in the breath. HAROLD L. HIGGINS. Johns Hopkins Univ. *Bull. Johns Hopkins Hosp.* **31**, 447-8(1920). —The method is based on that of Scott-Wilson (*C. A.* **5**, 3837). The air is collected in a rubber bag of 1000 cc. capacity (a football bladder is satisfactory). If possible the patient should blow up the bag as one does a toy balloon. A mask and valves may be used with babies or unconscious patients or the patient may breathe back and forth several times from a bag containing air, as in the Plesch method of obtaining alveolar air. The results with alveolar air are about twice those obtained when valves are used, but this is unimportant for diagnosis as the method does not have to be absolutely quant. and the differences may be allowed for. When detns. are being made on the same person from day to day, the same method of collection should be used. The bag should be washed out with 1000 cc. of air following the detn. Within 30 secs. after collecting the specimen, blow the air through a tube, similar to that in Polin's method for microdetn. of NH_3 , into 25 cc. of the Scott-Wilson acetone reagent contained in a large test-tube (30 X 200 mm.) ($\text{Hg}(\text{CN})_2$ 10 g., NaOH 180 g., H_2O 1200 cc.; shake in a flask, add 400 cc. of a 0.7268% soln. of AgNO_3 and decant from the ppt. which tends to form). The l. of air is blown through the soln. in about 30 secs. The white cloud reaches its max. density in about 5 min. Prepare a standard soln. of acetone containing approx. 5 cc. per l. and standardize by Messinger titration. This soln. will keep for months. From it prepare a dild. soln. by dilg. 5 cc. of the standard to 1 l. lcc. = approx. 0.02 mg; this soln. should be made fresh every 2 days. To 25 cc. of Scott-Wilson reagent in a second tube add 1, 5, 10, or 20 cc. of the dild. standard according to the amt. of acetone in the air being tested. Det. the amt. of acetone present by comparing the clouds in the tubes. The detn. can be made more accurate by dilg. the tubes with known or unknown amts. of acetone with H_2O until approx. the same cloudiness is present in both, and calcg. from the vols. of fluids in the two tubes and the amt. of acetone in the standard. A nephelometer may be used. A normal person will show no acetone and the soln. will remain clear; 0.02-0.05 mg. per 1000 cc. of air is a trace; 0.1 mg. a moderate amt., 0.2 mg. a large amt., and 0.4 mg. a very large amt. The detn. is of practical value in the following conditions: (1) in patients with hyperpnea when acidosis is recognized or suspected where it is important to know immediately if acetone bodies may not be the

cause of the condition; (2) in diabetic patients in diagnosing coma and in following the patient's condition when coma is impending or when changes in diet are being made; (3) as a guide to the condition in patients getting little or no food as in fasting or recurrent vomiting. The acetone content of the blood and of the alveolar air are proportional so that the detn. of the acetone in the breath gives a rough index of the amt. in the blood.

A. P. LOTHROP

A laboratory method for the preparation of fibrinogen. JAY McLEAN. Johns Hopkins Univ. *Bull. Johns Hopkins Hosp.* 31, 453(1920).—A readily sol. pptd. fibrinogen is obtained by salting out fibrinogen with $(\text{NH}_4)_2\text{SO}_4$ instead of NaCl. It will dissolve after 3 repts., and it is thus possible to obtain a product free from prothrombin, which tends to adhere to the ppt. The method is as follows: Carefully pour or pipet off the clear plasma from cat or dog blood, oxalated and centrifuged for 20 min. Add $\frac{1}{4}$ its vol. of satd. $(\text{NH}_4)_2\text{SO}_4$ soln. and promptly centrifuge for 5 min. Pour off the supernatant fluid. Carefully wash the ppt. at least twice by layering over it $\frac{1}{4}$ satd. soln. of $(\text{NH}_4)_2\text{SO}_4$. Add to the washed ppt. a vol. of 2% NaCl soln. equal to that of the original plasma and stir gently until dissolved. Filter. Ppt. and centrifuge as before. Pour off the supernatant liquid and drain. Wash for some min. in $\frac{1}{4}$ satd. $(\text{NH}_4)_2\text{SO}_4$ soln. and drain. Wipe the inside of the centrifuge tube with filter paper. Dissolve in 1% NaCl soln. and filter. Usually 2 ppts. are sufficient but the process may be repeated a third time. The soln. should clot in a few min. on adding thrombin or prothrombin and Ca and should not clot either spontaneously or on the addition of CaCl_2 . Fibrinogen prepd. by using NaCl has time and again failed to go into soln., whereas fibrinogen prepd. from the same plasma, but pptd. with $(\text{NH}_4)_2\text{SO}_4$, dissolved rapidly.

A. P. LOTHROP

Estimation of the phenolic substances in urine. FREDERICK F. TISDALL. Johns Hopkins Univ. *J. Biol. Chem.* 44, 409-26(1920).—"The results obtained for the total phenolic substances in urine by the Et_2O extn. method described are at least 50% lower than those recorded by Folin and Denis. There are substances in the urine, at present unidentified, which react with the phenol, uric acid, and blood-sugar reagents devised by Folin and his collaborators. These compds. are partly present in the free state and partly formed by the action of strong mineral acids on the urine. Whether they are simple conjugated bodies or chem. compds. formed by the action of strong mineral acids on some constituents of the urine has not been detd. It is suggested that these compds. may be responsible for the high values obtained for the phenolic substances in urine by the method of Folin and Denis. Only a small fraction of the volatile phenols are excreted in the urine in the free state." *Detn. of free (non-conjugated) phenols and aromatic hydroxy acids.* Shake 5 cc. of urine for 5 min. with 100 cc. of Et_2O . Sep. the urine and make 2 more extns., using 50 cc. of Et_2O each time. Shake the 200 cc. of Et_2O for 5 min. with 20 cc. of 10% NaOH soln., sep., neutralize the NaOH and make slightly acid with concd. HCl. Add Na_2CO_3 and the phenol reagent and compare the color produced with a standard phenol soln. according to the method of Folin and Denis (*C. A.* 9, 3263). *Detn. of aromatic hydroxy acids.*—Ext. a duplicate sample of urine with Et_2O and treat the ext. with 20 cc. of 20% Na_2CO_3 instead of NaOH. The difference in the amt. of color developed is a measure of the free phenols present. The urine samples should be preserved with CHCl_3 and used immediately on completion of the 24-hr. period as the hydroxy acids are rapidly converted into *p*-cresol and phenol the urine is allowed to stand. *Detn. of total phenols.*—Deconjugate exactly as directed by Folin and Denis (*C. A.* 9, 3263) and ext. with Et_2O as described above. The extn. may be carried out on the urine directly after heating with HCl, but the use of Folin and Denis' second filtrate is preferable as the soln. does not tend to adhere to the sides of the separatory funnel. The amts. of phenols found by this method correspond

very closely with values obtained by the methods of Mooser (*C. A.* 4, 1623) and Hensel (*C. A.* 6, 3436).

A. P. LOTHEP.

Accurate determination of urea in serum and other fluids by xanthidrol. W. MESTREZAT AND MILLR. MARTHE-PAUL JANET. *J. pharm. chim.* 22, 369-78(1920); cf. following abstr.—In the method of Fosse, Robyn and François (*C. A.* 8, 3803), exact results are obtained only if (1) the urea content of the liquid employed is brought to 0.5-1 g. per l. preferably to 0.5 g.; if (2) the amt. of xanthidrol (A) used is twice that of the F. R. and F. method; i. e., the amt. of 10% MeOH soln. of A should be 0.1 the vol. of the AcOH-urea soln. Mix 10 cc. of properly dild. serum with 10 cc. of strong Tanret's reagent (*C. A.* 8, 3803) and centrifuge. To 15 cc. of the clear mixt. add 15 cc. glacial AcOH, and after 10 min. each time, 3×3 cc. of freshly prepd. 10% MeOH soln. of A. After 3 hrs., pptn. of xanthylurea is complete (the slight solvent action of Tanret's reagent is compensated by the doubling of the amt. of A). Sep. the crystals, wash with a few cc. of abs. MeOH, then dry and weigh. In test expts., about 99% of the amt. of urea employed was recovered. The use of pure A and pure MeOH is essential.

S. WALDBOTT

Determination of urea in blood. Present state of the question. M. LAUDAT. *J. pharm. chim.* 23, 5-15(1921); cf. *Compt. rend. soc. biol.* 83, 730, 1023(1920); also cf. preceding abstr.—The xanthidrol method gives exact results, but requires delicate operations. The amt. of xanthidrol (A) should be 1.5 to $2 \times$ the theoretical; for low concns. of urea (less than 0.1%), the vol. of the A soln. should be 0.1 that of the mixt. contg. the urea. From 98.2 to 100.5% of urea employed was recovered by this method. Results were uniform also with decreasing amts. (10 cc.-1 cc.) of the same serum used, if due time was allowed for crystn. of the A-urea compd. The NaBrO method (cf. Grimbert and L., *C. A.* 7, 2588, 2763) is simple of operation, but has a source of error in evolution of O (up to 0.3 cc. O for 6 cc. of reagent); the error is minimized by using Meillère's reagent (*C. A.* 4, 462). Owing to the presence of uric acid, purines, creatine and NH_4 salts, L. finds that this method, with normal subjects under a mixed diet, gives results 25% too high, based on the A method. In cases of renal troubles, the excess is only 3 to 6.7%; but in hepatic disorders, it is as high as 75%. Thus the NaBrO method has a decided clinical value, especially in cases of renal affections.

S. WALDBOTT

Analysis of the gastric contents obtained by the fractional method. SYDNEY W. COLE AND W. J. ADIE. *Lancet* 1921, I, 423-6.—This is a report to the Medical Research Council and includes a discussion of the following points: the nature of the meal; the method of expressing results; the detn. of "free" acidity; the detn. of "total" acidity; the detn. of total and mineral chlorides, and thus of the active and combined HCl; the detn. of the enzymes present.

E. B. FRNK

C—BACTERIOLOGY

A. K. BALLS

Methylene-blue as indicator in determining the toxicity of phenol and phenol-salt solutions towards yeast. CHAS. G. FRASER. Univ. Toronto. *J. Phys. Chem.* 25, 1-9(1921).—The technic of prepg. pure cultures of *Saccharomyces cerevisiae*, wort-free cells, wort and wort-agar is given, as well as the method of prepg. a suspension of the proper count, using a Thoma chamber. The toxicity of 0.6% PhOH was compared with that of weaker PhOH solns. containing varying amts. of NaCl, using staining with methylene blue as an indication of death, according to the method of Fraser (cf. *C. A.* 15, 872). It was found that a soln. containing 2.0 g. NaCl and 0.53 or 0.54 g. PhOH in 100 cc. is isotoxic with 0.6% aq. PhOH. The "death-point" of yeast cells was detd. also by mixing the cells with the poison and then plating. Using the inability to form colonies as a criterion of death, the solns. containing NaCl are more toxic than those without salt. The chem. equivalents of the solns., calcd. from equil. detns. using kerosene and toluene as immiscible liquids, according to the method of Miller

(cf. C. A. 15, 120) were found. The results show that the PhOH solns. are isotoxic with their chem. equivalents containing NaCl, according to the first method, but that if colony formation is used as the death criterion, the solns. containing NaCl are more toxic.

A. L. BARKER.

The effect of alcohol on the toxicity of phenol towards yeast. ELLIS I. FULMER. Univ. Toronto. *J. Phys. Chem.* 25, 10-8(1921); cf. preceding abstract.—Yeast cells allowed to grow in a wort culture until a certain amt. of alc. is produced were more resistant to PhOH than normal cells. Addition of alc. to the media produces the same result. Alc. shows no toxic effect if the concn. is 4.0% or less, while in 8.0% alc. there is a decided increase in the no. of cells stained with methylene-blue. Chem. equivalents of dil. PhOH solns. (0.4 to 0.75%) containing 0, 3.75 and 7.5% alc. have been detd. by equil. expts. using toluene as immiscible solvent. If failure to produce colonies on agar be taken as sign of death, solns. containing H₂O, PhOH, and 3.75% alc. are more toxic than their chem. equivalents containing no alc.; if staining with methylene blue be used as sign of death, they are isotoxic. The latter method is recommended as being more accurate. Solns. of 8.0% alc. are still more toxic and solns. containing H₂O, PhOH, and 7.5% alc. showed more rapid increase of stained cells than chem. equiv. solns. of aq. PhOH.

A. L. BARKER.

Cresols and substitutes for cresol soap. III. Cresotates as solvents for cresol. E. HALLER. *Arch. Reichsgesund.* 52, 670-95(1920); C. A. 14, 2008; 15, 1033.—The purpose was to discover a suitable substitute for cresol soap, for use as a general disinfectant, more particularly, however, for military uses. The results obtained after extended expts. show the effect of various combinations of the cresotinic acids (Na salts) with cresol (Ger. Pharm.) toward staphylococci and other organisms (typhus, paratyphus, pyocyanus, etc.). One of the basic mixts. used was "Kresotin-Kresol," and consisted of Na *o*-cresotinate 20, H₂O 30, and Ger. Pharm. cresol 50 parts, which, as a rule, proved superior to corresponding dilns. of cresol soap. IV. Methods for testing the germicidal value of cresols. *Ibid* 695-726.—Comparative expts. are described for the purpose of evaluating substitute preps. for cresol soap, in order to clear up certain discrepancies existing between H.'s findings and those of other investigators.

W. O. E.

Physiology of yeast. ERICH KÖHLER. *Biochem. Z.* 111, 17-29(1920); cf. C. A. 15, 289, 408.—A study was made of enzyme consumption and supply, using the activity of a yeast suspension on maltose as the index of reaction. The course of the curve is detd. by the ratio between the enzyme consumption and the enzyme supply. Other observations indicated that where the products of enzyme activity accumulate growth of the yeast is impossible. K. is of the opinion that the enzymic action takes place in the outer regions of the plasma of the yeast cells.

F. S. HAMMETT.

Inhibitory action of *Calendula* upon bacterial growth and multiplication. ALBERT E. HINSDALE AND S. N. LORD. Ohio State Univ. *J. Am. Inst. Homeopathy* 13, 747-53(1921).—The *Calendula* prepn. was obtained by boiling dried tops of the marigold in distd. water until a satd. soln. of the sol. constituents was obtained. This soln. was used as such and in various dilns. *Calendula* was found to be a mild antiseptic, and to be practically bactericidal both *in vitro* and *in vivo* when used in a half-satd. soln. This action was exerted in an alk. environment. *Calendula* was without action on proteases.

JOSEPH S. HERBURN.

Utilization of nitrogen and of phosphorus in the mycellium of *Aspergillus niger*. W. VONBRODT. *Bull. acad. polonaise sci. lett., classe sci. math. et nat.* B 1919, 71-109.—In cultures of *Aspergillus* containing NH₄NO₃ as the source of N, loss and not fixation of that element occurred; the ammoniacal N was used in preference to the nitrate N, although a portion of the latter was also utilized. The % of total N and of the differ-

ent groups of nitrogenous compds. present in the mycelium depended essentially upon the amt. of nitrogenous nutrients present in the medium. Spores were produced more rapidly in cultures poor in NH_4NO_3 than in cultures containing that salt in greater concn.; H_3PO_4 exerted a similar influence upon the formation of spores: Org. nitrogenous compds. were not secreted into the nutrient soln. during the normal development of the mold; these compds., especially NH_3 , appeared in that soln. as products of the decompn. of the mycelium as a result of the degeneration of the mold. The amt. of N present as insol. protein in the mycelium, which grew in a soln. rich in both N and P_2O_5 , showed merely insignificant variations during the growth; therefore, the mold attempted to accumulate a considerable store of these proteins as rapidly as possible. The sol. protein represented an intermediate stage of metabolism in the mycelium; the % of these proteins present in the mycelium varied considerably according to the compn. of the medium. The proportion of NH_3 present in the mycelium during its normal development was extremely small. The proportion of nitrogenous compds. not pptd. by phosphotungstic acid, and particularly of amino acids, varied considerably according to both the stage of development of the mold and also the compn. of the nutrient medium. The *Aspergillus* withdrew NH_3 from the nutrient soln., and synthesized from it amino acids, polypeptides, and finally proteins. Inorg. P_2O_5 appeared in the mycelium even when the mold suffered from lack of P; it then played a limiting role in the mycelium. Sol. org. compds. of P were present in the mycelium in very variable amts. and represented transitory products. The P present as protein was the most stable (form of that element in the mycelium and varied the least in amt. The absorption of N from the nutrient medium, and its successive transformations in the mycelium depended to a large extent upon the amt. of P_2O_5 in the medium; these transformations were more uniform when the amt. of P_2O_5 was small than when it was larger. At times, the increase in insol. N and the increase in protein P ran parallel to each other during the growth of the mold. When the amt. of P_2O_5 in the nutrient medium was decreased, the % of total P_2O_5 in the mycelium began to decrease, next became const. and was then accompanied by a decrease in the amt. of dry matter produced. The ratio of the protein P to the insol. protein N varied within very wide limits according to the P_2O_5 content of the nutrient medium. The following amino acids were isolated from the mycelium in the free state: alanine, leucine, tyrosine and, probably, phenylalanine and proline.

JOSEPH S. HEPBURN

Bile powder in culture media for the demonstration of typhoid bacilli in water and in the blood. H. TOYODA. *Kitasato Arch. Exp. Med.* 2, 219-35(1918); *Jap. Med. Literature* 5, 36(1920).—To 100 cc. of the water under examn. are added a sterile soln. containing 1 g. peptone, 2.5 g. Na_2SO_4 , 0.5 g. NaCl and 10 cc. H_2O ; the resulting soln. is incubated for 8 hrs.; then a sterile soln. of 3 g. powdered, desiccated ox bile in 8 cc. H_2O and 1 cc. of a sterile aq. soln. of crystal violet (0.1 g. in 100 cc.) are added; after incubation for 10 to 16 hrs., the resulting soln. is sown on Endo plates. By this technic *B. typhosus* can be detected regularly in water containing as few as 10 of these organisms per 100 cc. With blood, 1 part of the sample is mixed with 2 parts of an 8 to 10% soln. of the powdered bile; and the mixt. is incubated. JOS. S. HEPBURN

Acid production by a new sulfur-oxidizing bacterium. S. A. WAKSMAN AND J. S. JOFFE. *Science* 53, 216(1921).—The authors isolated a strong oxidizer of S to H_2SO_4 which accumulated to large amts. even in the absence of neutralizing substances. The organism is autotrophic, deriving its energy from S oxidation; org. substances, however, are not detrimental. C for building protoplasm is derived from atm. CO_2 . In a medium entirely free of org. materials, and carbonates, and containing ammonium salts as sources of nitrogen and some inorg. minerals, S is rapidly oxidized. Formation of acid was detd. by titration and by the concn. of hydrogen ions. At the start the culture has

a reaction of $p_N = 5.6$, or an equivalency of 0.16 cc. 0.1 N alkali per cc. At the end of 85 days, this had changed to $p_N = 0.58$ and an equivalency of 4.00 cc. 0.1 N alkali per cc. A detailed study of this organism is promised in the near future in *Soil Science*.

F. W. TANNER

Sulfur bacteria. MARCKS. *Mikrokosmos* 14, 27-30(1921).—A general discussion of sulfur in its relation to *stream pollution* and the groups of organisms which force it through its cycle. The *Beggiatoa* are discussed and shown to have much significance in changing sulfur compds. No expl. data are given. F. W. T.

Action of ultraviolet rays on the Saccharomycetes. B. FEUER AND F. W. TANNER. *J. Ind. Eng. Chem.* 13, 285-286(1921).—The *Saccharomycetes* used in this investigation were destroyed in several min. Cf. *C. A.* 14, 2651. F. W. T.

ROBERTS, JAY G.: **Manual of Bacteriology and Pathology for Nurses.** Third revised Ed. London: W. B. Saunders. For review see *Modern Med.* 3, 69(1921).

D—BOTANY

CARL L. ALSBERG

A comparative study of the composition of the sunflower and corn plants at different stages of growth. R. B. SHAW AND P. W. WRIGHT. *Bur. Animal Ind. J. Agr. Res.* 20, 787-93(1921).—Solids, total and albuminoid protein, reducing and non-reducing sugar and starch data are recorded for 7 different growth periods. The solids showed a marked increase, while the total and albuminoid protein and the reducing and non-reducing sugars decreased during growth. The starch in the corn plant increased from 1.5 to 24% of the total solids while the non-reducing sugars showed a variable percentage, although the initial and final figures were identical. The starch content of the sunflower was comparatively low and variable, although the final figure was higher than the initial one. The solids of the mature corn plant averaged much higher than for the sunflower plant and the protein and carbohydrate constituents recorded in the table account for 40% of the solids in the former and for 13.5% of the solids in the latter plant. In both plants more reducing than non-reducing sugar was usually found. The chief difference in the 2 plants at the silage stage lies in the amt. and character of the carbohydrates. The best stage of maturity for ensiling the sunflower plant is when the rays of the flower have become dry and are falling. F. C. COOK

Recent advances in science—plant physiology. WALTER STILES. Univ. College, Reading. *Sci. Progress* 15, 383-7(1921).—Review of recent work on *permeability*.

JOSEPH S. HEPBURN

Lignified cell membranes. P. CASPARIS. Univ. Basel. *Pharm. Monatshefte* 1, 121-60(1920).—A summary is presented essentially as follows: A new reaction is described depending in all probability on the adsorption of a soln. of $\text{Co}(\text{CNS})_2 \cdot 4\text{H}_2\text{O}$ with the formation of a blue color (the soln., which contains 15-40% of reagent, and is violet-red to violet in color, is applied to a section carrying lignified membrane. The lignified cell walls are colored blue, the other elements remain uncolored, while the liquid appears bright red in thin layer.). In an extended series of expts. the reaction is studied in connection with Maule's KMnO_4 test, as also with the phloroglucinol reaction. All 3 differ markedly from one another, the new test being by far the most sensitive and dependable for lignified membranes. The adsorptive capacity for $\text{Co}(\text{CNS})_2$, as also for other salts, acids and bases, particularly those regarded as nutrient salts of the plant, is detd. quantitatively and compared with that for cellulose. Whereas the adsorptive capacity for the new reagent is considerably increased in the case of lignified membranes, the application of other salt solns. may be followed by hydrolysis with positive or negative adsorption. These phenomena are susceptible of demonstration as regards the upward movement of solns. in the natural H_2O ducts of the plant. Increased surface action of the trachea and tracheid channels arising from lignification

may be regarded as a physiol. function, which appears to restrain the basic components of nutrient solns. It is shown that Maule's test is only characteristic of lignin commonly present in angiosperms, and consists of 2 phases, an oxidation and chlorination. This test is, therefore, closely related to the "chlorsulfite" reaction of Cross and Bevan. The $\text{Co}(\text{CNS})_2$ test is least dependent on lignin as such, being mainly a colloidal reaction. In the case of plant membranes, the test points with certainty to lignification. Lignified cell walls do not consist of chemically homogeneous material; furthermore, an incrustation with lignin through adsorption of material by the membrane from without is improbable. It appears more likely that intramolecular formation of lignin takes place from the carbohydrates originally present in the cell wall. W. O. E.

Action of light on the sugar content of the beet. H. COLIN. *Bull. assoc. chim. suc. dist.* 38, 61-74(1920).—A review of the present conflicting opinions is given and the difficulty of isolating the light factor when conclusions are drawn from field crops is pointed out. Expts. were carried out on two successive years. Three adjacent plots 8-9 m. square were planted in the same manner with the same seed. One plot was left exposed to the light, a second shaded with thin cloth, and the third with thicker cloth. Pictures of the shelters and of some of the resulting beets are given. The wt. of the entire plant was much greater when it had been grown in the direct light, as was also the ratio of the wt. of the root to that of the leaves. The larger roots contained a lower percentage of sugar, but when the greater yield is considered it amounts to about the same yield of sugar for a given plot of ground. It is more desirable to the industry to have smaller beets of greater richness. This should be controlled by selecting the variety best adapted to each locality. C. concludes that if beets reach a high sugar content in a hazy climate, it is due not necessarily to the effect of the diffused light, but to all accompanying factors. The light of *l'Île de France* does not hinder the phenomena of assimilation and the storage of sugar. He believes that sufficient pptn. is the chief contributing factor to these processes. I. D. GARARD

Influence of clear weather on beets. ZAMARON. *Bull. assoc. chim. suc. dist.* 38, 74(1920).—A note. Part of a field of 2500 sq. m. was shaded about 7 hrs. daily. Beets from this section were compared with others from the sunlit portions of the field. The av. wt. of the plants grown in the direct sunlight was 0.806 kg; those from the shade 1.4. The av. for the roots, however, was 0.520 and 0.566, resp. The first averaged 15.42% and the second 10.42% sugar. The quotient of purity for the first was 81.1 and for the latter 71.0. I. D. G.

Hemicellulose of apple wood. W. E. TOTTINGHAM, R. H. ROBERTS AND S. LEPKOVSKY. *Univ. Wisc. J. Biol. Chem.* 45, 407-14(1921).—"Analysis of apple wood from fruiting branches shows a high content of the acid-hydrolyzable material commonly designated as hemicellulose. The EtOH-sol. fraction resulting from partial hydrolysis of this material contains large amts. of xylose and glucose, with a little galactose. It is suggested that this hydrolyzable material forms a reserve source of carbohydrate in the metabolism of the apple tree." I. GREENWALD

Reserve food materials in vegetative organs. G. M. TUTTLE. *Bot. Gaz.* 71, 146-51(1921).—A number of trees, shrubs and perennial herbaceous plants of the region round Edmonton, northern Alberta, were examd. Sections of leaf, stem and bud were tested with iodine soln. and osmic acid. Microchemical tests for sugar by means of the Flücker reaction (Tunmann, *Pflanzenmikrochemie* 1913) showed its presence in *Syringa*, *Populus*, *Prunus*, *Salix*, *Shepherdia*, *Ribes*, *Picea*, *Pinus*, *Rosa*, *Pyrola*, *Cornus* and *Eleagnus*. All the species examined showed a high starch content during the summer, which disappeared during October. With the exception of *Lonicera glaucescens* and *Crataegus* sp., all the trees and shrubs contained oils and fats as food reserve during winter. BENJAMIN HARROW

Chemical and physiological study of mottling leaves. F. M. SCHWARTZ. *Bot. Gaz.* 71, 81-130(1921).—Loss of chlorophyll by plant organs, natural enough in the autumn, is considered a diseased condition if it occurs during the growing season. In the latter case it is spoken of as "mottling" or "chlorosis." Morphological examn. shows that in the green leaf—S. examined *Coleus* leaves—the chloroplasts are large and blue-green, and one to three or more starch grains are visible; whereas in the mottled leaf the chloroplasts are yellowish, fewer in number, much smaller, with no green tint, and without starch grains. S. grew his plants in the purest fine quartz sand, in new 4-inch flower pots. During the course of the experiments the sand was watered with nutrient solns. bearing all the necessary elements for plant nutrition, or lacking either Ca, Mg, P, Fe or N. Twenty-six plants were used in each of the six sets, making 156 in all. The complete nutrient soln. was made up according to Pfeffer (as described in Duggar's *Plant Physiology* 1911), and the various solns. deficient in one or the other element were prepd. as suggested by Duggar. Cuttings were made of the plants, and rooted in sand for two weeks. The freshly potted plants were watered first with the nutrient solns. and then every morning with distd. water. About every week another application of the nutrients was made. The plants were grown from May 1 to Aug. 1. The effect of the lack of nitrogen was evidenced in four or five days by a noticeable yellowing. At the end of three months the plants with complete nutrient soln. and those without Ca, Mg or Fe, grew about equally well. "There was evidently enough of each of these elements already in the cuttings to care for considerable additional growth." All these plants were decidedly green. The dwarfed condition of the plant was striking in the absence of either PO_4 or NO_3 . In the absence of PO_4 the plants were still green, but when NO_3 was lacking, the color showed a great diminution of the chlorophyll content of the plant. With the exception of the plants lacking NO_3 and PO_4 , all showed branches developing in axils of the leaves. The branching was especially prominent in the plants lacking Fe. To eight of the plants (2½ months old) which were grown in sand cultures with NO_3 or PO_4 lacking, one watering was made with a soln. which contained the lacking element. Two weeks after the watering the height of the treated plants was about twice that of those which had no nitrate or phosphate added, and the area of the new leaves was 3-4 times that of the old. The plants to which nitrate was added showed noticeable greening in 4-5 days, and later became a normal green. Palladin's assertion that carbohydrates are essential to the formation of chlorophyll (*Plant Physiology. Engl. trans.* 1917) is probably true for etiolated *Coleus* leaves, but S. claims that the case of mottled leaves cannot be explained on this basis. S. kept young *Coleus* plants in darkness until the leaves became etiolated. "These etiolated leaves, when floated on distd. water in the light, remained yellow, those on KNO_3 soln. died, while those on a 5% sugars soln. greened slightly. On the other hand, *Coleus* leaves which had mottled in the light did not green again when floated on any of these solns." The decreased catalase content of mottled leaves may be a factor in preventing chlorophyll formation. The green leaves gave tests for nitrates, but no positive results were obtained with completely mottled leaves. More iron was found in the mottled than in the green leaf. While the quantity of chlorophyll *a* and *b* decreased with the increase of mottling, the quantities of carotin and xanthophyll increased.

BENJAMIN HARROW

Studies of photosynthesis in marine algae. 1. Fixation of carbon and nitrogen from inorganic sources in sea water. 2. Increase of alkalinity of sea water as a measure of photosynthesis. BENJAMIN MOORE, EDWARD WHITLEY AND T. ARTHUR WEBSTER. *Proc. Roy. Soc. London [B]* 92, 51-60(1921); cf. *C. A.* 14, 2359.—Marine algae are able to fix elementary N from water (therefore, indirectly from the atm.) in the presence of sunlight, but not in darkness. For fixation of C, use is made of the bi-

carbonates of Ca and Mg which are present in sea water; as fixation of C progresses, the sea water becomes more alk.; the limit of alkalinity is attained when all bicarbonates have been converted into carbonates; at this point, the H-ion concn. has fallen below the value pH 9.1. The degree of alkalinity favors acceleration of cell division and also induces abnormal and varying forms, during the strong sunshine of spring and summer. Marine algae which are grown in a limited vol. of water and a limited supply of air in sunlight and full daylight rapidly fix both C and N, and convert them into org. compounds. The amt. of N which is fixed exceeds many fold the original total N content of the water (including NH_3 , NO_2 ion, and NO_3 ion); moreover, the small amt. of each of these forms of N originally present in the water is not decreased. Therefore, the only available source of N is the free or elementary N of the atm.

JOSEPH S. HEPBURN

The osmotic concentration and electrical conductivity of the tissue fluids of ligneous and herbaceous plants. J. ARTHUR HARRIS, ROSS AIKEN GORTNER AND JOHN V. LAWRENCE. *J. Phys. Chem.* 25, 122-46(1921); cf. *C. A.* 15, 250, 1035.—Results are given of detns. of the osmotic concn. of the leaf tissue fluids of many species of plants from the Arizona deserts, a Jamaican montane rain forest and the mesophytic habitats of the north shore of Long Island. The sp. elec. cond. of the samples from the last named habitat is also given. A statistical discussion of the extensive data leads to the following conclusions: The osmotic concn. as measured by the cryoscopic method is far higher in the leaf tissue fluids of ligneous than of herbaceous species. The sp. elec. cond. of the leaf tissue fluids of ligneous species is lower than that of herbaceous species. The data supporting the former conclusion are so extensive and varied as to leave no doubt of its validity. Data from more varied habitats, bearing on the latter conclusion, are desirable.

T. G. PHILLIPS

Chemical mechanism of the assimilation of carbon dioxide by green plants. P. MAZÉ. *Compt. rend.* 172, 173-5(1921); cf. *C. A.* 15, 1035.—In this mechanism NH_2OH plays a fundamental role. The presence of this base is evident from the transformation of NH_3 into O compds. of N and *vice versa*. The principal intermediate compds. may be indicated thus: $HNO_2 \rightleftharpoons HNO \rightleftharpoons NH_2OH \rightleftharpoons NH_3$. Existence of NH_2OH is indicated also by the constant presence of free HNO_2 and frequent presence of HCN , both of which are derived from oximes formed by the union of NH_2OH with aldehydes and with ketones. NH_2OH may fix CO_2 as CO_2NH_2OH and $CO_2NH_2OH \rightarrow CH_2OH-CHO + HNO_2$, these products existing in the green leaves of the elder. With CH_3-CHO the CO_2NH_2OH gives $CH_3CHOH-CHO$ and HNO_2 as found in poplar leaves. The nitrifying action is represented as follows: $2[3HNO_2 + H_2O + CO_2 + O] \rightarrow 2[CO_2 + NH_2OH + 2HNO_2 + O] \rightarrow CH_2OHCHO + 6HNO_2$, the necessary energy being furnished by the oxidations. Solar energy may produce the reaction $HNO_2 + H_2O \rightarrow NH_2OH + O_2$. In these and other reactions it appears that the ratio $O_2:CO_2 = 1$.

L. W. RIGGS

Accessory factors to the growth of lower plant forms. PIERRE GOY. *Compt. rend.* 172, 242-4(1921).—Expts. with *Saccharomyces cerevisiae*, *Aspergillus niger* and various other fungi, also bacilli, led to the conclusion that vitamins are not indispensable to the lower plant forms; however, their evolution is to some extent influenced by an org. substance which G. has isolated in a cryst. form from cultures of *Mucor mucedo* in synthetic media. This compd. acts only after being heated to 85-90° and loses its properties at about 170°. It presents none of the characters of the amino acids.

L. W. RIGGS

Chemical examination of the wood of an old Amati violin. CARL G. SCHWALBE AND ERNST BÜCKER. *Z. angew. Chem.* 33, I, 272(1920).—The violin was 260-280 years old. The wood appeared to be that of *Picea excelsa*. Comparative analyses on

the "Amati" wood and a sample of wood used in modern violin manuf. disclosed few noteworthy differences. The ash and resin content of the old wood appears to be appreciably higher than that of the recent wood, but S. and B. are careful not to draw any conclusions from these differences.

LOUIS E. WISE

E—NUTRITION

PHILIP B. HAWK

NORMAL

Nutrition in Vienna; a study of the food supply and state of nutrition of the working classes in Vienna. MADGE R. GIBBON AND MARGARET I. H. FERGUSON. *Lancet* 1921, I, 474-7.—This investigation includes a study of the following points: (1) Energy intake of the diet. (2) Height and weight of individuals. (3) Income and expenditure. (4) Nature of the food material consumed. (5) Nature and extent of help given by relief agencies. (6) Rickets. These studies show the inadequacy of the diet of the working classes in Vienna at the present time. It is hopeless to expect from a population on such diets the initiative and vigor by which alone the country can be saved from ruin.

E. B. FINK

The influence of aeration on the stability of the antiscorbutic factor. S. S. ZILVA. *Lister Inst. Lancet* 1921, I, 478.—This preliminary note describes the results obtained from some expts. instituted with the object of studying the influence of air on the antiscorbutic factor at ordinary temp. and at 100°. This is an outcome of observation that ozone inactivated this and the fat-sol. factors at ordinary temp. The expts. revealed that bubbling air at ordinary temp. through an antiscorbutic soln. inactivated it. On boiling an active soln. for two hrs. in an atmosphere of CO₂, however, no marked diminution in the activity could be recorded, while on boiling a similar soln. for 1 hr. during which time air was bubbled through almost the entire activity was lost.

E. B. FINK

Influence of rations restricted to the oat plant on reproduction in cattle. E. B. HART, H. SYENBOCK AND G. C. HUMPHREY. *Univ. Wis. Agr. Exp. Sta., Res. Bull.* 49, 22 pp. (1920).—A ration composed of 7 parts rolled oats and 7 parts oat straw was found to be inadequate as a diet for breeding cows. The offspring were invariably born prematurely, and either were very weak at birth or were born dead. The value of the ration for reproduction was not improved by adding extra fat-sol. vitamins (butter) or casein, or both. The addition of Ca salts in the form of wood ashes, or Ca acetate or phosphate greatly improved conditions for reproduction, and offspring of fair vigor were obtained. Much better results were secured by the use of natural roughage, e. g., corn stover, clover, alfalfa, or marsh hay. The authors conclude that Ca was the principal deficiency in the above expts. The results indicate that the ration of a dry breeding cow should contain at least 0.45% of CaO, calcd. on the basis of the total ration, when the other factors are adequate.

A. L. BARKER

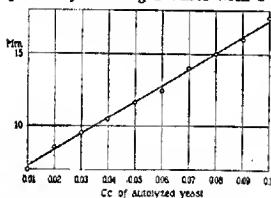
Results of nutritional surveys in U. S. training camps. JOHN R. MURLIN. U. S. Army. *Trans. Coll. Physicians, Philadelphia* [3], 41, 149-54 (1919).—The winter ration of the U. S. troops in France contained over 5000 cal. per man daily. In the army, the total daily consumption of food per man averaged 3633 cal. Each man required approx. 400 more cal. during the period October to March than during the remainder of the year. The caloric intake at mess bore no relation to the additional caloric intake at the canteen. The number of articles of food used in the mess of private soldiers in a training camp ranged from 50 to 55, and decreased to about 15 in the field; the officers' messes showed a much greater variety; the number used in civilian families is about 39. Very strict mess discipline was not inconsistent with good physical results, one regiment showing an av. gain of 6.6 lbs. per man in 5 months' training.

JOSEPH S. HEPBURN

Fermentation in the hulls of rice. K. KIRUJO. *Chuo Igakkai Zasshi* No. 273, 1148(1918); *Jap. Med. Literature* 5, 30(1920).—The amt. of acid produced during fermentation is greater in unpolished rice (containing the hulls) than in polished rice; the hulls facilitate growth of the acid-forming bacillus of fermentation. The increased indican content of the urine in beriberi is attributed to abnormal putrefaction in the intestine; this putrefaction could be inhibited by including rice hulls in the diet, and thereby stimulating acid fermentation in the intestine. JOSEPH S. HEPBURN

Calcium metabolism, also the role of the endocrine glands in dental formation and deformation. J. MADISON TAYLOR. Temple Univ. *Dental Cosmos* 63, 227-30 (1921).—A discussion of the role of the adrenals, thyroid, parathyroids, and thymus in Ca metabolism. JOSEPH S. HEPBURN

A test for anti-beriberi vitamine and its practical application. CASIMIR FUNK AND HARRY E. DUBIN. N. Y. *J. Biol. Chem.* 44, 487-98(1920).—The method is simple and rapid and appears to be applicable for a quant. detn. A yeast suspension is prepd. by shaking a loopful of a 48-hr. pure yeast culture in 100 cc. of Nāgeli soln. on a shaking machine for 3 hrs. Duplicate sets of ordinary bacteriological test-tubes are prepd. containing (1) 4 cc. yeast suspension, 5 cc. Nāgeli and 1 cc. H_2O ; (2) 1 cc. unknown vitamine soln., 5 cc. Nāgeli and 4 cc. H_2O ; (3) 1 cc. unknown vitamine soln., 5 cc. Nāgeli and 4 cc. yeast suspension. The tubes are incubated for 20 hrs. at 30° and the fermentation is then stopped by heating the tubes to 75° in a water bath for a few min. The contents are transferred to special centrifuge tubes, the bottom part of which ends in a capillary 2.5 cm. long and divided into mm., making the transfer quant. by washing 4 times with 1-cc. portions of H_2O . The air is forced out of the capillary by means of a wire half the size of the capillary and the wire washed with a few drops of H_2O . The tubes are centrifuged for 15 min. at 2,500 r. p. m. and the reading on the capillary is made without much delay. Sterility during the entire process, excepting centrifugation, is of paramount importance. With the capillaries used the controls were practically const. at 3.5 mm. and tests which did not give readings of at



least 4.5 mm. were considered to indicate the absence of vitamine. By using varying amts. of autolyzed yeast as a source of vitamine and as standard a curve was established by which it is possible to approx. the vitamine content of an unknown substance in terms of the standard, autolyzed yeast. The method is sensitive to 0.0001 cc. of autolyzed yeast, but the test is best arranged so that the amt. of unknown substance used corresponds to 0.05 cc. of autolyzed yeast, since in the interval between 0.01 and 0.1 cc. of autolyzed yeast the curve climbs abruptly and small differences can easily be read. If the test yields a too voluminous growth of cells, the soln. being tested should be dild. so that the amt. taken for a test (1 cc.) will give a result readable on the chart. Variation of the amt. of yeast suspension (0.5-5.0 cc.) has a very little effect on the final result. The method is of use in detg. the approx. vitamine activity only as inhibitory substances are present and not only the vitamine content but also the amt. of inhibitory substances may vary. A negative result may simply mean the presence of inhibitory substances but a positive result very likely indicates the presence of B vitamine. The abs. quant. estn. of the vitamine content of any product is possible only if the factor of inhibition can be removed or obviated. Using the method described, the following substances were found to show activity: urine, desiccated thyroid, pituitary ext., corn and wheat germ, corn and wheat minus the germ, orange juice. Among the substances showing no activity were leucine, tryptophan, allantoin,

hydantoin, nicotinic acid, a mixt. of 10 purine and pyrimidine bases, a mixt. of 6 amino acids, aq. ext. of codliver oil, autoclaved meat ext., starch, Crisco or lard. A study was also made of the effect of fractionation of autolyzed yeast ext. on its vitamin content. The activity was reduced about 50% after manipulation for 12 weeks through a series of 4 pptns. (with Pb acetate, HgSO₄, Ag acetate, and HgCl₂), a diazotization, and a reduction, together with unavoidable small losses at every stage. "The many manipulations speak well for the stability of the anti-beriberi vitamin under various conditions."

A. P. LOTHROP

A quantitative method for the determination of vitamin in connection with determinations of vitamin in glandular and other tissues. FREDERICK K. SWOBODA. Univ. Chicago. *J. Biol. Chem.* 44, 531-51(1920).—The biological test of Williams (*C. A.* 13, 2390) has been so modified as to be of quant. value for the detection of small amts. of H₂O-sol. vitamin. A count is made of the number of yeast cells developing in hanging-drop cultures from one or two single yeast cells after incubation at 30° for 18 hrs. The original should be consulted for a description of the details of procedure. The method has been used to det. the relative vitamin content of various organs. The H₂O-sol. vitamin is present in large amts. in most of the organs of internal secretion which are of developmental importance. The highest amts. were found in the pituitary and pineal glands. The suprarenals, testes, ovaries, and thyroid contain about the same amt. per g. of dried tissue. The liver and kidney are also high in vitamin content. Little is present in the thymus, pancreas, and lymph glands, all of which contain much nuclear material. It is possible that the vitamin is present in the pancreas in the form of vitaminogen, from which the active growth-promoting substance may be liberated by the action of acids or possibly enzymes; the high content reported by other investigators might be accounted for on this basis. The sciatic nerve contains a remarkable amt. of vitamin. Without proper diln. vitamin activity of thyroid ext. cannot be observed as it contains a substance toxic to yeast cells in addition to the growth-promoting vitamin. The anterior lobe and pars intermedia of the pituitary gland are rich in vitamin, but the content of the posterior lobe is relatively low. "The finding of vitamin in all these organs seems to indicate the importance of vitamin for growth or sex development. Whether this vitamin is a growth-promoting substance, *i. e.*, whether it facilitates the building up of the animal body in general only, or whether it is particularly a sex-promoting substance, remains to be detd."

A. P. LOTHROP

ABNORMAL

Infantile scurvy. JOHN AIKMAN. *Arch. Pediatrics* 38, 40-51(1921).—A review.

JOSEPH S. HEPBURN

Diabetes in children. STEPHEN H. BLODGETT. *Arch. Pediatrics* 38, 73-7(1921).

—Diabetes in children is usually of pancreatic origin; the urine has a sp. gr. of 1.020 to 1.045, contains a very slight trace or no albumin, from 20 to 500 g. sugar, considerable to very large amts. of acetone, and frequently diacetic acid. It may, at times, be accompanied by an infectious nephritis. The treatment depends on control of the diet, without recourse to a starvation diet. Diabetes of hepatic origin rarely occurs in children; its treatment likewise is by control of the diet. JOSEPH S. HEPBURN

Effect of certain dietary deficiencies on the suprarenal glands. C. H. KELLAWAY. *Proc. Roy. Soc. London (B)* 92, 6-27(1921).—Enlargement of the adrenals with an increased store of adrenaline occurs in pigeons which have been kept on a diet of polished rice. These changes still occur if either protein or fat be added to the ration, but are prevented by the addition of an adequate amt. of yeast ext. However, addition of yeast ext. to a basal ration of polished rice plus extra fat or protein prevented enlargement of the glands, but not the increased store of adrenaline. Enlargement of

the adrenals may possibly be due in part to congestion and edema of the glandular tissues, and in part to storage in the adrenal cortex of lipins liberated by the breaking down of body tissues; while a well marked cholesterolemia occurs in polyneuritic pigeons, nevertheless the cholesterol content of the adrenals in such diseased birds, as compared with normal birds, does not support this theory of lipin storage. When cholesterol is fed to rabbits and pigeons, hypercholesterolemia occurs, apparently associated with a slight increase in the adrenaline content of the adrenals. The increased store of adrenaline in the adrenals of birds on deficient diets is due to a decreased output of this compd. as a result of lowered body metabolism. Daily administration of adrenaline to birds on a normal diet and to those fed polished rice does not produce edema, and neither accelerates nor retards the onset of polyneuritis in birds on the latter ration; therefore, the edema which is noted in some cases of exptl. polyneuritis is not due to an increased output of adrenaline.

JOSEPH S. HAZBURN

Studies on creatinine metabolism. III. The excretion of creatine and creatinine during defervescence. MAX BÜRGER. *Kiel. Z. exp. Med.* 12, 1-27 (1921); cf. *C. A.* 14, 965.—The studies of creatine-creatinine during diseases with a short febrile course have shown that the febrile hypercreatininuria and creatinuria behave the same as during long periods of pyrexia, diseases where the temp. drops by crisis and artificial hyperpyrexia. In all these febrile conditions the ratio of creatinine N to total N is remarkably const., in contrast with the normal behavior, except when N excretion is greatly reduced. An exception was found in the case of artificially heating the muscles (diathermy), in which only the total creatinine N was increased. If several febrile attacks follow after short intervals or if pyrogenic substances are injected in rapid succession the creatine and creatinine values are reduced in the later periods of pyrexia. The explanation of the febrile hypercreatininemia and creatinuria is an increased flow of blood through the muscles plus the transformation of a precursor of creatine (creatinogen) into creatine with a secondary hypercreatinemia, creatinuria and creatininuria. Creatinuria is not a necessary accompaniment of febrile processes. Its occurrence during short febrile attacks indicates that it is not a phenomenon of inanition.

E. B. FINK

Pellagra in the mountains of Yancey Co., N. C. G. A. WHEELER. *U. S. Public Health Repts.* 1920, reprint No. 619.—Typical cases of pellagra were observed in Yancey Co., which has the highest elevation of any county in the eastern U. S. It is shown that these cases originated within the county, and that the usual dietary deficiencies existed, either because of unavailability of food for economic reasons or because of individual peculiarities in diet.

A. L. BARKER

Recent work on pellagra. CARL VORGTLIN. *Public Health Reports* 35, 1435-52 (1920); also issued as reprint No. 597.—A Harvey Society Lecture. The following conclusions are reached. No direct proof exists that pellagra has ever been transmitted experimentally in man or to animals. Direct proof supports the hypothesis that a causal relation exists between pellagra and a restricted vegetable diet. In pellagra, definite changes from the normal metabolism occur, and indicate decreased gastric secretion and increased intestinal putrefaction. Diet is the essential factor in the treatment and prevention of this disease; an appropriate change in diet suffices as a preventive without any change in the other sanitary conditions. A diet of the compn. used by pellagrins prior to their attack by the disease produces malnutrition and certain pathological changes in animals, similar to those occurring in pellagra; however, typical pellagrous dermatitis has not been observed in animals. Continued consumption of a restricted vegetable diet has produced pellagrous symptoms in man. While the nature of the dietary defect has not been discovered, certain observations point to a combined deficiency in some of the well recognized dietary factors as the

cause of the pellagrous syndrome. A bibliography of 46 references is appended.

JOSEPH S. HEPBURN

Influence of vitamins on the course of pellagra. CARL VORGTLIN, H. M. NEILL AND ANDREW HUNTER. *U. S. Public Health Ser. Hyg. Lab. Bull.* 116, 7-35(1920).—Protein-free exts. were obtained from liver, thymus gland, yeast, and rice polishings. The exts. from the animal organs probably contained a greater variety of the accessory substances (vitamins), although they were poorer in antineuritic substances than the yeast and rice-polish exts. The latter exts. were highly efficient for the prevention of avian polyneuritis, and were very potent in relieving symptoms of that disease in birds which had been kept on an exclusive diet of polished rice. However, these exts. (yeast and rice-polish) generally failed to modify the course of the disease when administered to pellagrous patients over a considerable period of time and in large amts. (based on the curative dose for fowls); one case was possibly an exception to this rule. The exts. from liver and thymus were administered to pellagrins, and produced an improvement in their condition apparently comparable to that produced by consumption of a diet rich in fresh animal proteins. "The evidence presented clearly indicates that the dietary defect responsible for pellagra is distinctly (qualitatively) different from and perhaps more complex than the one causing fowl polyneuritis and human beriberi."

JOSEPH S. HEPBURN

Occurrence of pellagra in nursing infants, with observations on the chemical composition of the human milk from pellagrous mothers. CARL VORGTLIN AND R. H. HARRIS. *U. S. Public Health Ser. Hyg. Lab. Bull.* 116, 73-97(1920).—A description is given of a case of pellagra in a breast-fed infant whose mother did not exhibit symptoms of the disease. Suggestions are made concerning the proper diet for pellagrous mothers and their infants. Chem. analyses were made of the breast milk from 5 cases of uncomplicated pellagra; no striking deviations in compn. from normal human milk were detected. Lactose, fat, total N, and total solids were within normal limits but below the av. Total ash and P_2O_5 content were normal. Cl and Na were present in larger amts. than normal. The % of Ca, Mg and K was slightly below normal. Casein and lactalbumin showed but a very moderate diminution. Tests were not made for the vitamin content of the milk, and it may possibly have been lacking in these compds. The total vol. of the milk frequently was greatly diminished. Both total N and non-protein N in the milk were apparently increased by a change from a low-protein to a high-protein diet. "The findings here reported do not conflict with the vitamin theory of pellagra, although no definite proof of this theory is furnished." J. S. H.

Recent advances in science (vitamins) (HAAS) 10.

F—PHYSIOLOGY

ANDREW HUNTER

Determination of relative activity of the thyroid lobes. N. WORTH BROWN. *Toledo. Endocrinology* 5, 29-32(1921).—The string galvanometer was used to register the action currents of the 2 lobes of the thyroid. Three cases are reported giving evidence of the possible utilization of this method of study in disturbances of thyroid activity.

F. S. HAMMETT

Transmission of physiological influence in nerve and other forms of living matter. RALPH S. LILLIE. *Clark Univ. Scientia* 28, 429-44(1920).—In protoplasm, as in other systems with an emulsion structure, the properties and behavior are determined by the nature of the interfacial films. These films, in protoplasm, have properties similar to those of the film on passive Fe, though markedly differing from the latter in chem. compn. Living protoplasm owes its characteristic chem. reactivity (irritability) and its power to transmit chem. influence to a distance to the chem. instability of these films and to their susceptibility to alteration under elec. influence. "A simple morg.

model resembling protoplasm in these respects would be a system consisting of numerous particles or filaments of passive Fe, arranged to form a coherent structure and permeated by an oxidizing soln. like HNO_3 . Such a system would be irritable, would conduct chem. influence between its different parts, and would return automatically to the original quiescent or resting state after each activation. Conceptions based on a recognition of these resemblances should suggest lines of exptl. investigation that will throw light upon many of the hitherto inexplicable properties of living matter."

JOSEPH S. HEPBURN

The relation between taste and circulation in the tongue. EMIL V. SKRAMLIK Freiburg. *Z. exp. Med.* 12, 50-4(1921).—A 20% grape sugar soln. placed upon the frog's tongue leads to temporary stasis of blood in the capillaries. Stronger solns. are even more effective. Quinine in 0.25% soln. produces an increase in blood flow and a fibrillary twitching of the musculature of the tongue. The action of quinine is antagonistic to that of sugar and immediately overcomes it. NaCl solns. in concns. of 4% produce a brief acceleration; solns. of over 10% cause complete inhibition which may be reestablished by quinine or washing with H_2O . Weak tartaric acid solns. (about 0.5%) increase the capillary circulation, even after quinine has been applied. Similar results were obtained with the mucosa of the stomach and intestine of the frog.

E. B. FINK

The influence of extract of the posterior lobe of the hypophysis upon the excretion of fluid by the stomach wall. HEINRICH HOFFMANN. Breslau. *Z. exp. Med.* 12, 134-42(1921).—The effect of pituitary gland upon the healthy stomach consisted of an increase in total gastric secretion, which was thinner, cloudy, practically free from mucus, trypsin and protein and containing only a trace of free HCl. E. B. FINK

Sir Thomas Richard Fraser. J. T. C. *Proc. Roy. Soc. London (B)* 92, pp. xi-xvii (1921).—Obituary notice, including an account of Fraser's contributions to biochemistry.

JOSEPH S. HEPBURN

A preliminary report on blood coagulation. E. C. MASON. Univ. Cinn. *J. Lab. Clin. Med.* 6, 195-9(1921).—Fibrinogen, Ca and a phospholipin complex enter into the process of clotting. Protective colloids may play a role in the prevention of clotting. Conditions which increase protective colloids, such as tissue autolysis, retard coagulation. Substances accelerating coagulation are of great variety, but have one point in common: they are electronegative. The protective portion of the phospholipin complex is apparently neutralized by these electronegative substances.

E. R. LONG

Effect of thyroid feeding and of thyro-parathyroidectomy upon the pituitrin content of the posterior lobe of the pituitary, the cerebrospinal fluid, and the blood. P. T. HERRING. Univ. St. Andrews. *Proc. Roy. Soc. London (B)* 92, 102-7(1921).—Exptl. material was obtained from adult cats of as nearly as possible the same age and body wt. Three sets of cats were used; each set consisted of 3 males and 3 females. One set served as normal controls; one set was fed the ordinary ration plus large amts. of fresh ox thyroid for 2 or 3 weeks. Thyro-parathyroidectomy was performed on the cats of the third set; the typical symptoms always developed; and the animal was killed from 3 to 6 days after the operation. Each cat was placed under anesthesia; the cerebrospinal fluid was collected from the fourth ventricle; the animal was bled, and the blood defibrinated; the pituitary body was obtained by dissection, and its posterior lobe separated. This lobe and the cerebrospinal fluid were dried separately as rapidly as possible at a temp. of 37°. For the physiol. tests, use was made of a 0.001% ext. of the dried posterior lobe in Ringer soln., and of a 1% ext. of the dried cerebrospinal fluid in Ringer soln. Neither thyroid feeding nor thyro-parathyroidectomy affected the pituitrin content of the posterior lobe of the pituitary body, as was shown by the

action of the exts. obtained from it upon the contraction of the isolated uterus of the virgin rat and upon the blood pressure of the pithed cat. No evidence was obtained of the presence of pituitrin in the cerebrospinal fluid of the fourth ventricle of either normal, or thyroid-fed, or thyro-parathyroidectomized cats; the exts. derived from this fluid were tested for their influence upon the rat uterus, and upon the blood pressure, kidney vol., and urinary secretion of the cat. The defibrinated blood from all 3 sets of cats showed no appreciable difference in action upon the rat uterus. The blood of thyroid-fed cats exerted a greater depressor action upon the circulation of the cat than did blood from normal cats. Blood of thyro-parathyroidectomized cats exerted a slight depressor action followed by a distinct pressor effect, which lasted for some time, on the circulation of the cat; the kidney showed a transient contraction; and the flow of urine was distinctly diminished. The defibrinated blood (3 cc.) was administered intravenously.

JOSEPH S. HEPBURN

Phagocytosis stimulated in citrated blood. M. OTANI. *Kiiasato Arch. Exp. Med.* 2, 147-218(1918); *Jap. Med. Literature* 5, 35(1920).—Virulent tubercule bacilli were used for the detn. of the opsonic index. Very little difference in this index was found between normal sera and tuberculous sera. However, when citrated blood and a suspension of the bacilli in 1.5% citrate soln. containing 0.85% NaCl were used for the detn., tuberculous blood showed very markedly increased phagocytosis, compared with normal blood. This reaction apparently was sufficiently const. and sp. to be of diagnostic value.

JOSEPH S. HEPBURN

State of the parathyroid glands after the destruction of the thymus by the injection of thymotoxic serum into the young dog. HIROTERU YOMAOKA AND MASAJIRO OGATA. *Acta. Schol. Med. Univ. Imperial Kyoto* 3, 391-400(1920).—Destruction of the thymus by means of thymotoxic serum does not give rise to any phenomena of either degeneration or regeneration in the parenchyma of the parathyroid glands, and does not produce any reaction in their blood vessels and connective tissues. These findings support the theory that the thymus and the parathyroids are independent of each other, both embryologically and physiologically.

JOSEPH S. HEPBURN

Senile changes in the respiratory organs. T. NAKANOIN. *Kyoto Igaku Zasshi* 15, No. 3, 153-63(1918); *Jap. Med. Literature* 5, 33(1920).—Degenerative changes occur in the elastic fibers, especially in the walls of the alveoli. These changes are due to deposition of fat and cholesterol-like compds. from the blood, in which their concn. increases with advancing age.

JOSEPH S. HEPBURN

Effect of endocrine derangement on the teeth. F. W. BRODERICK. *Bourne-mouth, Eng. Dental Cosmos* 63, 135-47(1921).—The ductless glands act on the dental tissues by means of their internal secretions, and, under normal conditions, bring about eruption, cause sufficient calcification previous to eruption and increased calcification after eruption, are concerned in the prevention of caries through their control of the alkalinity of the saliva, produce arrested decay if caries occurs, and possibly exert a trophic action to maintain the tooth tissues in a healthy state able to resist caries. Evidence was obtained that the alkalinity of the saliva—both total alkalinity as detd. by titration with 0.01 N H₂SO₄ and methyl orange, and H-ion concn. as detd. by means of bromocresolpurple and phenolsulfonephthalein—and its Ca index were decreased in certain diseases such as measles, scarlet fever, and phthisis, and were increased by administration of a pluriglandular prepn., containing exts. of the suprarenal, anterior lobe of the pituitary, and either thyroid or preferably parathyroid glands, accompanied by Ca lactate.

JOSEPH S. HEPBURN

Changes in the biological character of red blood cells after long preservation in vitro. S. SOOHN. *Tokyo Igakkukai Zasshi* 32, No. 18, 1-16(1918); *Jap. Med. Literature* 5, 38(1920).—Rabbit erythrocytes were preserved in a sugar soln. containing the

citrate ion, and showed no trace of hemolysis for 5 or 6 weeks. Their O-consumption was: 36% after 48 hrs., 66% after 10 days, complete after 3 weeks; their O-capacity had decreased approx. 13% after 3 weeks. The vol. of the cells increased slightly up to the 10th day, and decreased again after the 40th day. The resistance to hemolysis by hypotonic NaCl soln., and the viscosity gradually increased, attained a max. on the 30th day, and decreased after the 40th day. The blood from a rabbit, which had been rendered chronically anemic, was characterized by very active O-consumption, the greater portion being used within 12 hrs.; this phenomenon was more marked after use of poisons than after bleedings; the O-capacity remained unchanged. J. S. H.

Placental permeability. I. The differential resistance to certain solutions offered by the placenta in the cat. R. S. CUNNINGHAM. Johns Hopkins Univ. *Am. J. Physiol.* 53, 439-56(1920).— $\text{Na}_4\text{Fe}(\text{CN})_6$ and Fe NH_4 citrate when injected intravenously into pregnant cats penetrate the ectodermic layer of the placenta in about 2 hours. After about 5 hrs. the $\text{Na}_4\text{Fe}(\text{CN})_6$ passes through the cell membrane adjacent to the fetal capillaries and can be detected very quickly in the fetal urine. No citrate has been able to pass out of the fetal ectoderm at this time nor even several hrs. later, despite the fact that it has unquestionably entered it. J. F. LYMAN

G—PATHOLOGY

H. GIDEON WELLS

Biochemical study of bacterial metabolism in its relation to changes in the denser tooth structures in the mouth. SAMUEL E. POND. *J. Nat. Dental Assoc.* 8, 146-56 (1921).—The optimum H-ion concn. was found to be at pH 4.5 for *B. acidophilus* and *B. bifidus* (acid group), and to be between pH 7.8 and 8.4 for *B. subtilis* and *Streptococcus viridans* (alkaline group). "These organisms appear to transform medium with considerable rapidity. The acid region is one where the constituents of the enamel and dentine are dissolved rapidly; but no such change is apparent, nor would be anticipated, in the alk. region indicated. The action of the organisms upon dentine, in an alk. region, does not appear to increase the amino acid N content, and this is true, likewise, of trypsin acting in a similar region. This tends to disprove the 'liquefaction of dentine' idea, as far as enzyme digestion in an alk. region is concerned." J. S. H.

Adrenaline hypersensitiveness in definite and unproved tuberculosis. FRED H. HEISE AND LAWRASON BROWN. Trudeau Sanatorium, New York. *Am. Rev. Tuberc.* 4, 600-15(1920).—The Goetsch adrenaline test (*N. Y. State J. Med.* 18, 259; *Am. Rev. Tuberc.* 3, 109(1919); cf. *C. A.* 14, 2219) was used in a series of 260 cases, 205 with pulmonary tuberculosis. Of the tuberculous cases 14% reacted to adrenaline. Of the non-tuberculous cases 29% reacted. When there was evidence of tuberculous activity, as shown by symptoms, X-ray or complement fixation, 10% reacted and when there were no evidences of activity, from 13 to 19% reacted. When tubercle bacilli were present in the sputum 10% and when absent 17% reacted. In 17% of the cases, having a history of hemoptysis of a dram or more, the reaction was positive. In no case with a history of pleurisy with effusion was the test positive. In 14% of the cases with a history of a dry pleurisy the reaction was positive. When the disease was of limited extent 27%, when moderate 15%, and when extensive 9% reacted. When the subcutaneous tuberculin test was positive in tuberculous cases 26% and when negative 20% reacted to adrenaline. In the non-tuberculous 25% of those reacting to the tuberculin were positive to the adrenaline test, and 40% of those not reacting were positive. None of the tuberculous colitis cases reacted, nne case of Pott's disease with previous thyroidectomy reacted and one (with central nervous involvement) of four cases of lues reacted. H. J. CORPER

Gold-sol reaction of normal and pathologic serum. JOSEF REITSCHÖTTER. Berlin. *Z. Immunität*. 30, 468-81(1920).—The gold-sol reaction is not characteristic of antibodies. Various antitoxic sera of the same species have a similar gold-sol. curve within the limits of exptl. error. Various bactericidal sera possess the same power of protecting colloidal gold as normal sera. The reaction is not species sp. and is detd. only by the constituents of the serum. The changes in the serum during immunization consisting in a diminution in its albumin content also decrease the gold-sol. value. It follows from this that the transformation products of the albumins as well as the euglobulins possess an increased protective power. The euglobulins contain a substance of unknown nature, which does not have the property of a protective colloid and, therefore, reduces the protective power of the euglobulin fraction. The albumins have the least gold-sol. value, the euglobulins the greatest, while the paraglobulins are intermediate. The gold-sol. reaction is of value in the diagnosis of infections only in so far as it demonstrates the presence of pathological changes in the diseased organism; it indicates nothing sp.

E. B. FINK

Does the blood of patients recovered from smallpox contain complement-binding antibodies, with vesicle lymph as antigen? CHANG CHIA PIN AND CHEN YÜ HSIANG. Shanghai. *Z. Immunität*. 31, 18-21(1921).—By the use of vesicle lymph as antigen, 50 persons (Chinese) who had recovered from smallpox were tested for complement fixation. Of these 45 gave a negative reaction, 2 were positive, 2 weakly positive and 1 doubtful. Age, sex, time elapsed since recovery (which varied in these cases from 2 to 43 yrs.), severity of the infection (as measured by the degree of scarring) furnish no criteria for predicting the outcome of the reaction.

E. B. FINK

Further studies on the value of diphtheria serum in treatment. R. KRAUS AND ST. BARCER. *Z. Immunität*. 31, 85-92(1921).—The curative action of diphtheria serum in animal expts. is influenced by individual factors in each animal. Under the same exptl. conditions a definite % of the animals could not be saved by increasing the dose of serum. Therefore, in human therapy an increase in action up to a max. quant. of serum may be expected, but a certain proportion cannot be saved by further injection of serum. Expts. on the prophylactic use of serum demonstrated a similar individual variation among animals.

E. B. FINK

Agglutination of dysentery bacilli by the serum of pregnant women. WALDEMAR LORWENTHAL. Bern. *Z. Immunität*. 30, 439-67(1920).—Serum obtained during labor gave a positive agglutination reaction with *B. dysenteriae*-Y in a large % of the cases studied. Since this % is much greater than the incidence of bacillary dysentery the explanation is either increased formation or greater activity of normal agglutinins. According to expts. with guinea pigs, pregnancy as such is unable to stimulate the production of agglutinins which had previously been present but had disappeared before conception. The provisional explanation that the increased cholesterol content of the serum during pregnancy strengthens agglutination must be abandoned. Numerous adequate expts. in which cholesterol or lecithin was added or the lipid content diminished by extn. showed that there is no definite influence of lipoids upon bacterial agglutination (in this connection a universal *extn. app.* is described). Theoretical considerations and exptl. studies of other serologic changes in pregnancy (Koltmann and Abderhalden reactions, antiproteolytic substances, meiotagmin reaction) or the assumption of an increased destruction of protoplasm does not offer a satisfactory explanation. Studies on the nature of acid agglutination show that in the presence of protein, dysentery bacilli are agglutinated in a lower H^+ concn. approaching that present in pregnancy, and that this "alkali agglutination" and sp. agglutination may supplement each other. However, the reduction in H^+ concn. during pregnancy is too slight to be of much influence, but it does illustrate that biophysical changes such as affect dysentery bacilli occur during pregnancy. The agglutination of *B. dysenteriae*-Y by

serum in pregnancy was found to run parallel with agglutination of red blood cells during pregnancy, which is dependent upon a lowering of the elec. charge.

E. B. FINK

Paragglutination. FRIEDRICH BREINL. *Prag. Z. Immunität.* 31, 1-17(1921).—Numerous strains of *B. coli* possess receptors homologous with the non-toxic dysentery groups, as long as they are kept in their natural environment. Receptors for the typhoid group are just as common. These homologous receptors are rapidly thrown off when the coli strains are grown on artificial media. Agglutination of certain coli strains does not indicate a sp. relation to disease processes in the intestines of individuals in whom these strains are normally present. The artificial cultivation of receptors is only a relative phenomenon and has nothing to do with the receptor apparatus of bacteria. "Paragglutination" in the sense of Kuhn and Woihte does not exist and the term should be dropped from the literature.

E. B. FINK

Complement fixation. E. WEIL. *Prag. Z. Immunität.* 31, 50-84(1921).—The activity of complement-binding antibodies against bacteria depends upon stable receptors of the bacteria, the labile being only of slight influence in the reaction.

E. B. FINK

Non-specific immunity. I. Precipitation and complement fixation following non-specific immunization. MAX PINNER AND IVAN IVANCHEVIC. Hamburg. *Z. Immunität.* 30, 542-59(1920).—By non-sp. immunization with air bacteria, guinea pig bile and pure tuberculin, sp. agglutinins and complement-binding antibodies for typhoid, dysentery, paratyphoid and proteus bacilli were obtained in rabbits. Minute doses (3 injections of about 1/100,000 oese) of Proteus X19 bacilli stimulated the production of agglutinins in rabbits.

E. B. FINK

Sensitization of ferric hydroxide sols by means of protein-free fractions of normal and immune serum. JOSEF RIRTSTÖTTER. Berlin. *Z. Immunität.* 30, 507-16(1920).—The sensitizing action of a number of electrolyte-free protein fractions upon Fe(OH)₃ sols varies in degree. All protein-containing Fe(OH)₃ sols are more sensitive to the coagulative action of electrolytes than pure Fe(OH)₃ sols; the sensitivity of albumin-Fe(OH)₃ sol is greater than that of paraglobulin sols. The paraglobulins of antitoxic sera possess a greater sensitizing action than the paraglobulins of normal or antibacterial sera and it may be concluded from this that antitoxins become negatively charged. It is possible to differentiate without animal expts., by purely physico-chem. methods, between antitoxic paraglobulins and normal proteins. Their sensitizing action on Fe(OH)₃ sols may be considered as a reaction with antitoxins.

E. B. FINK

The fetal and placental theories of eclampsia. ERWIN ZWEIFEL. Munich. *Z. Immunität* 31, 22-49(1921).—In all serologic and anaphylaxis studies the technique employed is of the greatest significance. The studies of Lichtenstein on the toxicity of the placenta are cited as an example. Freund reported a series of rabbit expts. in which intravenous injections of placental exts. regularly proved fatal, while subcutaneous and intraperitoneal injections were without effect. Lichtenstein found that the animals died only when the placental tissue was passed through a No. 5 sieve. When a finer sieve such as No. 6 was used the animals remained well, indicating that death was due to the injection of coarse placental particles. The writer's expts. on guinea pigs and rabbits prove that the considerations upon which is based the theory that eclampsia is due to sensitization with fetal and placental protein have no basis in fact. A sensitivity to fetal or placental protein of the same species does not exist. The theory that eclampsia is an anaphylactic reaction against fetal or placental protein of the same species, based upon purely speculative grounds, must be abandoned.

E. B. FINK

Specific precipitation by the combination of alcohol-soluble "sheep receptors" of organs with their antibodies. F. GURN, Frankfurt. *Z. Immunität.* 30, 517-41 (1920).—The antibodies of the so-called "sheep blood receptors" in the organs of the guinea pig, horse, etc., have a pptg. action upon the alc. exts. of such organs as well as sheep blood. The reaction is dependent upon a sp. antigen-antibody reaction, because, in contrast with sheep blood and guinea pig kidney antiserum, normal rabbit serum and the serum of other species do not possess pptg. action; pptn. occurs with guinea pig kidney ext. but not with rabbit kidney ext.; the pptg. antibody is bound by sheep blood but not by beef blood. There is a definite but not very marked parallelism between the sheep blood hemolytic amboceptor content of sheep antisera and their pptg. activity. The most marked differences occur between sheep and heef blood antisera in that only the former ppt. while both contain more or less sheep blood amboceptor. The specificity of the pptg. reaction is reduced at low temp. At room temp. large quantities of antiserum produce non-sp. pptn. and the sensitivity of sp. pptn. is considerably reduced. Non-sp. ppts. obtained at low temps. disappear upon raising the temp., whereas the sp. ppt. increases under similar conditions. A definite NaCl content favors pptn. The addition of guinea pig serum reduces pptg. activity and the reduction is more marked with active than with inactivated serum. The exts. of various organs differ in sensitivity. Guinea pig kidney exts. are most sensitive, while liver exts. are least sensitive. The active principles of organ exts. resist boiling even in alc. solns. dild. with normal NaCl soln. The pptn. reaction may be used to detect *horse meat products* in a manner similar to the Sachs-Georgi amboceptor binding method.

E. B. FINKE

The cerebrospinal fluid in disseminated sclerosis. DOUGLAS KINCHEM ADAMS. Glasgow Univ. *Lancet* 1921, I, 420-2.—The cerebrospinal fluid in multiple sclerosis possesses the following characteristics: a normal cell count, a negative Wassermann reaction, a luetic or paretic reaction to colloidal gold, and in most cases (83%) a normal protein content. On the supposition that the origin might be spirochetal, treatment was carried out with spirochetal drugs. In practically every case modifications toward a negative result of the colloidal gold reaction were noted. As regards clinical effects of such treatment, no improvement resulted in advanced cases of the disease, but prolonged treatment produced amelioration of early cases, and in one or two instances the results were marked.

E. B. FINKE

The standardization of tuberculin. A. J. EAGLETON. Wellcome Res. Lab. *Lancet* 1921, I, 429-31.—The following factors must be controlled if accurate results are to be obtained: the same strain of tubercle bacillus must be used for injecting the animals; the guinea pigs should be about the same size; all animals to be given injections of tuberculin should be examined and any sick ones discarded—no animal should be used unless the inguinal glands are palpable; the von Pirquet test should be used to guide the dosage for subcutaneous injection. The results show that the tuberculins can be tested with a reasonable degree of constancy. They also show the value of the von Pirquet test as an adjunct to the subcutaneous test. Work is being done on the standardization of a purified, dried tuberculin, which may, if found satisfactory, be used as a standard in future work.

E. B. FINKE

Anaphylaxis studies. LX. Further studies on the supposed production of anaphylotoxin with starch and inulin and the physical theory of anaphylotoxin formation. E. FRIEDBERGER. *Z. Immunität.* 30, 275-320 (1920).—Normal guinea pig serum treated with starch and inulin followed by centrifugalization does not give reactions which are in any way comparable with true anaphylaxis or anaphylotoxin. Such mixts. do not produce local necrosis on subcutaneous injection and do not pass through the pores of earthenware filters. True anaphylotoxins are filterable and produce a sp. symptom complex upon injection into animals.

E. B. FINKE

Anaphylaxis studies. LXI. Does anaphylotoxin represent a phase of auto-precipitation of serum globulins (Dold)? E. FRIENBERGER AND E. PUTTER. *Z. Immunol.* 30, 321-50(1920).—This investigation concerns the statement of Dold that anaphylotoxin is produced by a pptn. phase of the serum globulins, studies of the optical behavior of anaphylotoxin mixts. and analogous expts. upon toxicity for the guinea pig. The conclusions of Dold based upon test-tube expts. were not confirmed on animals. Animal expts. also fail to show any relation between pptn. phenomena and primary toxicity of sera. E. B. FINK

A serological study of the bacillus of Pfeiffer. VI. ARTHUR F. COCA AND MARGARET F. KELLEY. Cornell Univ. Med. Coll. *J. Immunol.* 6, 87-101(1921).—An immune serum prepd. by the injection of one strain of *B. influenzae* was found to agglutinate other strains of that bacillus, but not the one used for immunization. This phenomenon was due to the presence of an unusual quantity of a sp. inhibiting antibody. E. B. FINK

Diurnal variations in the hemoglobin content of the blood. GEORGES DREYER, H. C. BAZETT AND H. F. PIERCE. Oxford Univ. *Lancet* 1920, II, 588-91.—The diurnal variations in hemoglobin % met with in men and animals may reach as high as 30%, while 10% changes are of common occurrence. In general, the excursions seem to be more marked in animals with a low hemoglobin content of the blood. In attempting to establish the normal hemoglobin content in a series of individuals it is essential to make observations at a time of day when the daily variations are found to be the smallest, *i. e.*, between 5 and 7 p. m. In the study of phenomena where alterations in the concn. of blood are concerned it is necessary to view them in the light of the marked normal diurnal variations that may occur. E. B. FINK

Active immunity in diphtheria. BRUNO BUSSON AND E. LÖWENSTEIN. Vienna. *Z. exp. Med.* 11, 337-48(1920).—Active and passive immunity may be produced in animals with neutralized and slightly over-neutralized diphtheria toxin-antitoxin mixts. If the mixts. are allowed to stand they increase in toxicity; under-neutral mixtures become more toxic, just neutral mixts. produce late death and paralyses. Immunity produced by this means occurs relatively late, is demonstrable after 20 days, and reaches a max. only after 3-4 mos. The quantity as well as quality of the mixt. influences the degree of immunity produced, larger quantities being definitely more efficient. Greatly over-neutralized mixts. produce no immunity. In the experience of the writers, mixts. slightly overneutralized and non-toxic for 250-g. guinea pigs in doses of 4.0 cc. are the most suitable for use. In the present state of our knowledge, under-neutralized mixts. are not safe. The action of the toxone which is undoubtedly set free in such mixts. needs further investigation. E. B. FINK

Disturbances in heat regulation following removal of the kidneys. E. P. PICK AND JULIUS SCHÜTZ. Vienna. *Z. exp. Med.* 10, 257-68(1920).—In the course of uremic intoxication there is a drop in body temp. Uremic animals during the height of the intoxication are poikilothermic in behavior, since they have lost in large measure the temp.-regulating ability against cold. Substances such as Mg and chloral hydrate, which produce a central narcosis, increase the temp. of uremic animals; doses of 0.03-0.08 g. $MgCl_2$ and 0.005-0.05 g. chloral hydrate per kg. animal suffice to produce a rise in temp and narcosis under these conditions. Tetrahydronaphthylamine and cocaine produce a rise in temp. only in animals suffering from severe uremia. Caffeine in one case had no temp. effect. The disturbance of temp. regulation in uremia is central and depends upon a narcosis of the heat center. E. B. FINK

Immunity and predisposition to diphtheria. JOHANNES SCHÜRER. Frankfurt. *Z. exp. Med.* 10, 225-56(1920).—The period of greatest susceptibility to diphtheria is between 3 and 5 years. The greater resistance of older children and adults cannot

be entirely due to an acquired immunity from an attack of diphtheria, since the active immunity in diphtheria is transient and the sp. antitoxin produced does not remain long in the body. The existing immunity is due rather to the presence of antitoxin in the serum resulting from chronic infection (diphtheria bacillus carriers). The absence of antitoxin in the serum indicates a constitutional defect. The antitoxin content of the blood is not a measure of the degree of immunity. The ability of the tissues to react against diphtheria toxin is frequently of greater importance. The hypersusceptibility of the tissues in man as well as exptl. animals may make it impossible for the antitoxic action of the serum to manifest itself. This increased susceptibility may be non-sp. (status lymphaticus, tuberculosis) and probably also sp.

R. B. FINK

The action of water-insoluble, organic and inorganic fine dispersoids upon blood cells, complement, amboceptor and upon the animal body. E. FRIEDBERGER AND E. PUTTNER. Greifswald. *Z. Immunität*, 30, 227-74(1920).—A series of fine dispersoids was found to be hemolytic for red blood cells. Different preps. of the same substance, such as kaolin, vary in the intensity of their action. Coagulated kaolin and argilla are almost non-hemolytic. With the exception of animal charcoal only inorg. substances are hemolytic. Inorg. substances that settle rapidly are not hemolytic. Of other inorg. substances, only those are hemolytic that are finely granular with sharp irregular surfaces. The action is probably a mechanical breaking up of the corpuscles which liberates the hemoglobin. Hypertonic solns. and temp. have no influence upon hemolysis. A series of fine dispersoids was also found to bind complement. Complement is bound less readily by coagulated than by uncoagulated substances. There was no relation between complement binding and hemolytic activity. In the case of some preps. there was a definite difference between complement fixation at 37° and 0°. Bacteria bind complement equally well whether alive or dead, at 37° or 0°. Another series of non-hemolytic substances bound complement only at 37°. Contact with *magnesia usta* reduces complement-binding power, probably by the production of complementoids or other complement-inhibiting substances. Hypertonic NaCl solns. inhibit complement fixation by adsorbents. The end piece (of complement) is also bound by adsorbents. Expts. with the middle piece present technical difficulties. The results of Sachs and Stilling (*C. A.* 14, 2024) with reference to the double function of inulin as complement binder and amboceptor as well as complement fixation by *B. prodigiosus* by the use of decreasing quantities of bacterial emulsions and varying amts. of guinea-pig serum could not be confirmed. Sp. amboceptor is more readily bound in dil. than in concd. solns. In their action upon amboceptor the different kaolin preps. also vary. Complementophile and amboceptorophile action do not run parallel; neither is there any relation between ability to bind amboceptor and hemolytic activity. Coagulated and non-coagulated kaolin possess the same effect upon amboceptor. The action is definitely reduced at 0°. If the amboceptor is dild. with normal serum instead of with normal NaCl soln. adsorption fails to occur. Suspensions do not bind amboceptor or complement in hypertonic NaCl solns., but the latter is bound by homologous corpuscles. Expts. to test the relative affinity of adsorbents and amboceptor for complement and adsorbents, and blood corpuscles for amboceptor, indicated that when blood, amboceptor, complement and adsorbent (bacteria) are mixed simultaneously, complement has a greater affinity for the adsorbent than for amboceptor, while when blood, complement, amboceptor and adsorbent (silicic acid) are simultaneously mixed the affinity of the corpuscles for the homologous amboceptor is greater than for the adsorbent. Kaolin proved to be bactericidal. Various adsorbents had no effect upon infusoria (paramecia). There was no demonstrable action upon the isolated intestine. Upon intraperitoneal injection of guinea pigs with ad-

sorbents toxic symptoms were produced, esp. fever; these were not explainable on the basis of binding of complement. The intraperitoneal injection of kaolin into actively prepared guinea pigs had no influence upon their anaphylactic behavior (through complement hindering); the absence of an increase in sensitivity is emphasized. An intraperitoneal injection of various adsorbents reduces resistance to bacterial (X_{18}) infection. This effect is not due solely to hindering of complement, since coagulated kaolin, which does not bind complement, possesses the same action. Neither can there be a question of mechanical injury by sharp fragments since talcum and inulin, which are smooth, have the same property as kaolin. E. B. FINK

Histological changes in the perfused liver. EMIL V. SKRAMLIK AND THEODOR HÖNERMANN. Freiburg. *Z. exp. Med.* 11, 349-66(1920).—Ringer soln., when used as a perfusion fluid, is injurious to the cells, esp. the protoplasm of the liver cells. The action of cobra venom is characterized by a complete destruction of the capillary endothelium. The protein demonstrable in the perfusion fluid is derived from the injured capillary walls and the Kupffer cells. The "organ binding" phenomenon consists of an agglutination of red blood cells in the capillaries, for which the Kupffer cells are probably largely responsible. The same explanation probably holds for the occurrence of bacterial agglutination following perfusion of agglutinins through the liver. E. B. F.

Bronchial asthma: response to pilocarpine and epinephrine. HARRY L. ALEXANDER AND ROYCE PADDOCK. Bellevue Hosp. and Cornell Med. Coll. *Arch. Intern. Med.* 27, 184-91(1921).—"In a series of 20 cases of bronchial asthma, a general examn. with routine lab. aids and drug tests revealed no constant associated condition. The most frequent finding was abnormally increased sensitiveness to pilocarpine. These cases frequently presented constitutional defects (status lymphaticus) and abnormal reactions described as characteristic of the condition called vagotonia. The majority of cases reacted also to epinephrine with an abnormal rise in blood pressure and other characteristic signs—pallor, tremor, sometimes rigor—denoting increased sensitiveness to this drug. A relation between low blood pressure and excessive epinephrine reaction was apparent, while the smaller no. of cases with normal or high blood pressures gave regularly normal reactions. Cases reacting excessively to epinephrine were found to be relieved by 0.25 cc., a much smaller dose of this drug than is usually employed." I. GREENWALD

Thiocyanate content of the saliva and urine in pellagra. M. K. SULLIVAN AND PAUL R. DAWSON. Pellagra Hosp., Public Health Service. *J. Biol. Chem.* 45, 473-88 (1921).—Saliva was collected from 18 patients on admission and at discharge. In the first series, the vol. of the 30-min. saliva varied from 21 to 84 cc., av. 47.7 cc.; KSCN in 30 min., 0.39 to 3.53 mg., av. 1.45 mg.; KSCN per 100 cc., 0.87 to 10.09 mg., av. 3.51 mg. In the second series, these values were 38-95, av. 58.8 cc.; 0.90-8.18, av. 2.77 mg., and 1.53-12.40, av. 4.66 mg., respectively. The 24-hr. urine of 14 patients was similarly examined. In active pellagra, the vol. was 455-2965, av. 1139 cc.; total KSCN 15.7-93.5, av. 53.7 mg.; KSCN per 100 cc. 1.07-10.07, av. 5.74 mg. When the patients were convalescent, the values were 1115-2240, av. 1586 cc.; 43.3-96.6 mg., av. 64.0 mg. and 2.42-7.67, av. 4.23, resp. "The increase of the 'SCN of the saliva and urine seems to be associated with the betterment of the general condition of the patient, with better assimilation, a higher protein metabolism, and presumably a greater detoxifying power of the system as a whole. The increase of the 'SCN of the urine at discharge, over that of entrance, however, is not proportional to the increase of the total N of the urine." I. GREENWALD

Blood volume in pernicious anemia. GEORGE P. DENNY. Harvard Med. School and Peter Bent Brigham Hosp. *Arch. Intern. Med.* 27, 38-47(1921).—Blood vol. was calcd. from the O_2 capacity of the blood before and after transfusion and of the

blood used for transfusion and the quantity of the latter used. In 10 cases of pernicious anemia, 19 detns. showed a vol. of blood lower than normal in all but 2 cases. The decrease is due to the reduction in the number of cells, the plasma vol. remaining the same. In one of the 2 cases showing a normal blood vol., detn. of cell vol. with the hematocrit showed that the plasma vol. was unusually large. This was probably true in the other case also. See following abstr.

I. GREENWALD

The constancy of the volume of blood plasma. A. V. BOCK. *Mass. Gen. Hosp. Arch. Intern. Med.* 27, 83-101 (1921); cf. preceding abstr.—Blood vol. was detd. by the use of the vital red method. In 5 normal individuals, the blood vol. (B. V.) in liters was between 7.6 and 9.1, average 8.79% of the body wt. in kilos and the plasma vol. (P. V.), 4.5-5.7, av. 5.1%. In 3 cases of polycythemia vera, B. V. was from 12.8 to 14.3, av. 13.2% and P. V. 4.7-6.1, av. 5.2%. In 7 cases of pernicious anemia, average B. V. was 5.7% and P. V. 4.9%. Of these, 4 with a hemoglobin content between 43 and 59%, gave a P. V. of 5.4%. Two others, in which the hemoglobin fell below 30%, P. V. was 4%. In 7 miscellaneous cases, including some with edema, B. V. varied from 4.7 to 8.2%, average 7.1% and P. V. from 4.0 to 6.0%, av. 4.9%. In 8 cases of diabetes, the values found were V. B. 6.0-8.9%, av. 7.3%; P. V. 3.7-6.2%, av. 4.8%. In 7 cases of edema (3 nephritis, 2 diabetes, 2 cardiac) B. V. varied from 4.7 to 9.1%, but P. V. only from 4.0 to 5.1%. After hemorrhage, plasma vol. is rapidly restored to normal if there is an adequate supply of fluid and if hemoglobin has not been reduced below 25%. Mention is made of the reports of others of a low blood vol. and great concn. of blood in cases of pulmonary edema, profuse sweating, diarrhea, etc.

I. GREENWALD

Thymic disease. A. E. SEIGEL. *N. Y. Med. J.* 113, 290-2 (1921).—A brief report, one of the conclusions of which is that the thymic secretion exerts a selective depressant influence on cerebral respiratory centers.

F. S. HAMMETT

Cellular immunity: observation on natural and acquired immunity to cobra venom. J. A. GUNN AND R. ST. A. HEATHCOTE. *Oxford Univ. Proc. Roy. Soc. (London) B* 92, 81-101 (1921).—*Natural immunity.*—When injected subcutaneously, the minimum

lethal dose of cobra venom per kg. of body wt. for the cat is 20 times that for the rabbit. When excized hearts of these animals were artificially perfused with Locke soln. to remove the serum, the soln. of venom required to arrest the cat heart was at least 4 times as concd. as that required to arrest the rabbit heart. The isolated intestine of the cat withstood the toxic action of higher concn. of venom than did the isolated intestine of the rabbit. Hence the natural immunity of the cat to cobra venom is at least partly due to a cellular immunity of the tissues of the cat. Cat erythrocytes did not possess this cellular immunity, and were actually more sensitive than rabbit erythrocytes to the hemolytic action of the venom. *Acquired immunity.*—After a rabbit had been immunized to cobra venom, its isolated heart and intestine, which had been perfused with Locke soln. to remove the serum, withstood higher concns. of the venom than did the same organs of a normal unimmunized rabbit. Therefore, during the process of acquired immunity, at least some of the tissues develop a cellular immunity, apart from the antitoxin (antivenom) which circulates in the serum. The serum-free erythrocytes from immunized rabbit showed an increased sensitiveness to the hemolytic action of the venom, and were lacking in cellular immunity. Therefore, the erythrocytes cannot be taken as a reliable index of cellular immunity in either natural or acquired immunity. The different behavior of the erythrocytes and the other tissues examd., with respect to cellular immunity, is possibly due to their different structure and life history. Evidence has been obtained that a cellular immunity of such tissues as the muscle of the heart and intestine can be produced.

JOSEPH S. HEPBURN

Alleged decrease in the thiocyanate content of the saliva in syphilis. FRANZ PETER. *Wiener klin. Wochschr.* 30, 595-6 (1917).—From a study of the saliva from

24 untreated cases and 57 treated cases of syphilis, Peter concludes that the thiocyanate content of the saliva does not decrease regularly in syphilis but is then merely subject to the same variations as in normal individuals.

JOSEPH S. HEPBURN

Recent advances in science—medicine. R. M. WILSON. *Sci. Progress* 15, 389-91(1921).—Review of recent researches bearing on immunity and infection.

JOSEPH S. HEPBURN

Origin of salivary calculus. HERMANN PRINZ. Univ. Penna. *Dental Cosmos* 63, 231-8(1921).—This, the first installment of the paper, is devoted to a review of the literature, and to a discussion of the various physico-chem. factors which may be concerned in the formation of salivary calculus.

JOSEPH S. HEPBURN

Excessive uricacidemia in gout and nephrolithiasis. A. CHAUFFARD, P. BRODIN AND A. GRIGAUT. *Presse Médicale* 28, 905(1920); *J. Am. Med. Assoc.* 76, 412.—The findings in 13 cases of gout and 21 with kidney stones showed a uric acid content decidedly above normal. This hyperuricemia with gout differs from that with nephritis, as with the latter the trouble is merely from retention, while with the former it is the result of deranged metabolism. In 3 dogs the uric acid content of the portal vein was much higher than that of the peripheral veins or the hepatic vein, indicating that the liver arrests the uric acid compds. When this uricolytic function of the liver is impaired, uric acid accumulates in the blood. This special form of insufficiency of the liver, associated with an excess of cholesterol in the blood, and sometimes with an excess of bilirubin, justifies the traditional role that has been assigned to the liver as a factor in gout. The kidneys suffer from these incompletely-transformed elements in the blood, and this sets up a secondary vicious cycle. A topbus examd. contained a large proportion of sodium urate and of cholesterol, showing the double adulteration of the blood serum, and its connection with the local lesions. Gout and gravel are thus both traceable to a common condition, the uricolytic insufficiency of the liver cell.

L. W. RIGGS

Stability of the acid-base equilibrium of the blood in normal and in naturally nephropathic animals. WM. DEB. MACNIDER. Univ. N. C. *Science* 53, 141-3(1921); cf. *C. A.* 14, 2951.—Expts. were made with 16 naturally nephropathic and 10 normal dogs, the latter serving as controls. The animals were anesthetized, a glass cannula was inserted in the femoral vein and connected with a buret whereby acid or alkali was introduced into the animal's circulation. At the end of 30 min. of etherization the reserve alkali of the blood from the saphenous or external jugular vein was detd. by the method of Marriott. The animals then received either 5 cc. per kg. of 0.5 N HCl or 25 cc. per kg. of 3% NaHCO₃ and the reserve alkali was detd. at 15-min. intervals during the first hr., and at 30-min. intervals during the final hr. When a normal animal receives intravenously an acid or alk. soln. there occurs a disturbance in the acid-base equil. of the blood which is temporary, and which is rapidly followed by a reestablishment of the animal's normal acid-base equil. With a naturally nephropathic animal subjected to a similar disturbance in the acid-base equil. of its blood, the lack of stability on the part of the mechanism which maintains this equil. is shown by the facts that the acid or alk. soln. induces a greater degree of variation from the animal's normal equil. and that the animal is unable to reestablish within the time limit allowed the normal animal a return to the blood to a normal acid-base equil.

L. W. RIGGS

Presence of calcium oxalate in tuberculous sputum. ALBERT AND ALEXANDRE MARY. Paris. *Mem. rev. soc. cient. "Antonio Alcala"* 38, 351-3(1920).—Chem. analysis of sputum from time to time in the "Institute de Biophysique" revealed the very frequent presence of CaC₂O₄. Microscopic preps. of sputum frequently contained the crystals, which in unstained preps. resembled those found in urinary sediment. Pulmonary excretions appear to be influenced both qual. and quant. by pathologic modifications of the metabolism, and by visceral diseases.

L. W. RIGGS

Blood formula with retention of chlorides. A. PAVCH. *Presse Médicale* 29, 35(1921); *J. Am. Med. Assoc.* 76, 620.—P. states that it is futile to test the blood serum for its NaCl content as the latter never changes, water being always retained to maintain the concn. at a constant level. Hence there is no diuretic so powerful as mere abstinence from NaCl. With retention of NaCl, there is also retention of water to correspond, but the dry residue of the blood, exclusive of the NaCl, is not increased. Consequently, the discovery of lesser concn. of the dry residue is a sign of abnormal retention of water, and thus indirectly, of retention of NaCl. This edema of the blood may long precede actual edema of the tissues. Whenever the NaCl content of the dry residue of the serum is found above normal, measures to ward off edema should be applied at once without waiting for further signs of NaCl retention. L. W. RIGGS

Bence-Jones proteinuria. WALTER WALTERS. *J. Am. Med. Assoc.* 76, 641-5 (1921).—A study of 3 cases with varying diets and analyses of blood, urine, saliva, bronchial secretions, and cerebrospinal fluid is reported. Conclusions: "A large quantity of albumin in otherwise negative urine in a patient with normal renal function and normal blood pressure and a marked secondary anemia should suggest the possibility of Bence-Jones proteinuria, especially when bone lesions are present. Bence-Jones proteinuria is significant from a diagnostic and from a prognostic standpoint of multiple myeloma, since it occurs in 80% of all cases and is usually followed by death within 2 years. The quantity of Bence-Jones protein excreted is independent of the protein intake, evidenced by an approx. constant excretion for 3-br. periods, irrespective of changes in diet. The amt. of Bence-Jones protein excreted during the night, when food is not taken, is only slightly less than the amt. excreted during the day. There is not a constant relationship between the quantity of Bence-Jones protein and the total urinary N excreted. As the finding of Bence-Jones protein in the urine led to its detection in the blood, it may be possible that other proteins of a similar or dissimilar nature are in existence in the blood and are not excreted by the kidneys."

L. W. RIGGS

Creatine and muscle tonus in man. FREDERICK S. HAMMETT. *J. Am. Med. Assoc.* 76, 502-3(1921).—Analyses of the blood of 2 patients indicated a condition of creatinemia coincident with the emergence from catatonic stupor when the normal muscle tonus is beginning to be reestablished. These results are interpreted as supporting the opinion that creatine is an end product of the catabolism of certain precursors in the protein mol. and particularly that phase of muscle-protein catabolism associated with the condition of muscle tonus.

L. W. RIGGS

Gastric analysis. II. Interdigestive phase or the principles governing the phenomena of the resting stomach. MARTIN E. REHFUSS AND PHILIP B. HAWK. *J. Am. Med. Assoc.* 76, 564-6(1921); cf. *C. A.* 14, 2506.—The following factors are characteristic of the interdigestive phase: (1) The av. normal residuum in health of the stomach during this phase is 50 cc. and this residuum in every instance has the qualities of a physiol. active secretion, hence the suggestion that the stomach is never inactive. (2) The total acidity averages 30 in terms of 0.1 N NaOH or less than one-half the total acidity of the digestive phase. (3) Pepsin concn. by the Mett method averages 3, again different from the digestive phase, and for low acidities was more or less parallel to total acidity. Trypsin by Spencer's method averages 7.1 units, and was inversely proportional to the total acidity. (5) Active regurgitation of the bile was noted in more than 50% of the cases. (6) The cryoscopic index was 0.47, indicating a tendency for osmosis of material from the blood into the lumen of the stomach. (7) Sp. gr. was inversely proportional to the total acidity, av. 1.0056. During the interdigestive phase motor function is totally altered. These facts are discussed in relation to pathologic conditions. In health a satisfactory balance is maintained be-

tween the digestive and interdigestive periods. In disease this balance is changed and the interdigestive period may be completely obliterated—a condition comparable to incompetence in other organs of the body.

L. W. RIGGS

Industrial tuberculosis and the control of the factory dust problem (WINSLOW, GREENBURG) 13.

H—PHARMACOLOGY

ALFRED N. RICHARDS

Importance of vanadium in therapy. J. MESSNER. *Pharm. Monatshefte* 1, 148-9 (1920).—An address.

W. O. B.

The significance of the acidosis of methanol poisoning. CHARLES C. HASKELL, S. P. HILEMAN AND W. R. GARDNER. *Arch. Intern. Med.* 27, 71-82 (1921).—The lethal dose of MeOH, administered by mouth or subcutaneously, to dogs was from 8 to 8 cc. per kg. A reduction in the CO₂ capacity of the plasma was generally observed but this was not proportional to the other evidences of toxicity, being sometimes only slight in fatal poisoning and at other times great with comparatively slight poisoning. The intravenous administration of NaHCO₃ was not effective in prolonging life and was, in itself, dangerous. The lethal dose of NaHCO₃ was sometimes smaller when given when the CO₂ capacity was low than when it was high. Two dogs with CO₂ capacities of 62 and 59.4%, respectively, received 5 cc. 10% NaHCO₃ per kg. and survived. On the following day, with CO₂ capacities of 52.6 and 57.4%, 4 cc. per kg. was fatal.

I. GREENWALD

Studies of hypnotics. PUYAL AND MONTAGUE. Lab. of Therapeutic Chemistry, Pasteur Institute. *Bull. soc. chim.* 27, 857-62 (1920).—The urethan series is characterized by high hypnotic value, low toxicity and absence of secondary effects. It would be ideal if a more active member were found than those commonly employed, viz., ethyl urethan and α -methylbutyl urethan (hedonal). α -Ethylpropyl urethan is less active, differing from the similar deriv. of barbituric acid (veronal). The introduction of the phenyl group into veronal increases its activity 4 times. Halogenation also increases activity. To study the effect of these substituents in the urethan series compds. of the type NH₂CO₂CHRCH₂CH₂Cl were prepd. by treating with NH₃ the chloroformic acid esters formed by the action of COCl₂ on the chlorohydrins produced by reaction of chloropropionaldehyde with organomagnesium compds., and compds. of the type NH₂CO₂CHPhR were prepd. by reduction of the corresponding ketones, by treating BzH with organomagnesium compds., or by treating aldehydes with PhMgBr. γ -Chloro- α -ethylpropyl urethan, long silky filaments from ligroin, m. 68°, sol. in 200 parts of water, sol. in most org. solvents, but little sol. in cold ligroin, is prepd. by adding drop by drop 300 g. ClCH₂CH₂CH₂OH (b. 173°) to 250 g. liquid COCl₂ in a flask cooled with ice and salt, letting the mixt. come to room temp., when gradually there is a liberation of gas, which rapidly becomes tumultuous, washing the mixt. with ice-water, sepg. the lower layer by decantation, drying over CaCl₂, distg. *in vacuo* (the chloroformate b₁₈ 95°), agitating with excess NH₃ in a flask cooled in ice, washing the white ppt. carefully with H₂O and recrystg. from ligroin. α -(β -Chloroethyl)butyl urethan, m. 68°, very similar to the above urethan, is prepd. by the same procedure from 230 g. COCl₂ and 250 g. ClCH₂CH₂CH₂PrOH (b₁₇ 90°). The intermediate chloroformate b₁₈ 110°. α -Methylbenzyl urethan, m. 78°. α -Ethylbenzyl urethan, fine spangles from a mixt. of C₆H₆ and petr. ether, solidifies 89°, very sol. in alc. and in benzene, 0.09% sol. in cold water, insol. in petr. ether, rather sol. in olive oil, is prepd. by adding with const. agitation, drop by drop, a mixt. of 135 g. PhCH₂OH and 200 g. PhNM₂ to 115 g. COCl₂ in 500 cc. PhMe cooled to 0°, letting stand at room temp. for 3 hrs., treating with crushed ice, decanting the PhMe soln., drying over Na₂SO₄, cooling, satg. with NH₃ (which forms a voluminous ppt. of NH₄Cl), washing with ice-water, then with

10% HCl, evap. the PhMe *in vacuo* and recrystg. from alc. at 60° or from a mixt. of C_6H_6 and petr. ether. α -Propylbenzyl urethan, solidifies 80°, is prepd. from the corresponding alc. (b_{11} 115-7°), made by the action of BzH on PrMgBr. α -Butylbenzyl urethan, m. 75°, is prepd. from the corresponding alc., b_{11} 120-5°. α -Ethylallyl urethan, needles from benzene-petr. ether, m. 73°, rather sol. in H_2O , of a very pronounced cool taste, is obtained from the corresponding alc. (b. 114-6°), prepd. in 50-6% yield from acrolein and EtMgBr. α -Vinylbenzyl urethan, m. 146°, from the alc. h. 215-6°, b_{11} 110-4°. β -Chloro- α -(ethoxymethyl)ethyl urethan, b_{11} 175°, m. 50°, is obtained from the alc. prepd. by heating $(CH_2Cl)_2CHOH$ with EtOH at 180°. The chloroformate may be prepd. with or without the presence of PhNMe₂. α -(Ethoxymethyl)- β -phenoxylethyl urethan, m. 72°, from the alc., b_{11} 165°, obtained by letting stand for 1 day a mixt. of $EtOCH_2CH(OH)CH_2Cl$ and PhOH with concd. NaOH. β -Chloroethyl urethan m. 76°. Cyclohexyl urethan, m. 110°, from the cyclohexyl chloroformate, b_{11} 78-83°. These urethans have been studied by Launoy, who will soon publish the results of his work.

H. C. HAMILTON

Paul Ehrlich. R. M. *Proc. Roy. Soc. London (B)* 92, pp. I-VII (1921).—Obituary notice, including an account of Ehrlich's contributions to biochemistry. J. S. H.

Pharmacological evidence of the action of the infinitesimal. ALBERT E. HINSDALE. *J. Am. Inst. Homeopathy* 13, 815-21 (1921).—Isolated strips of smooth muscle from the upper portion of the duodenum of rabbits were mounted in 175-cc. portions of oxygenated Locke soln. at a temp. of 38°. Each segment was then subjected to the action of a definite concn. of eserine, which was added to the Locke soln.; triplicate tests with different strips of muscle were made with each concn. of the eserine. Very marked stimulation of the muscle was produced by concns. of eserine as low as $1/2000$ grain in 175 cc., marked stimulation by concns. as low as $1/2000$ grain in 175-cc., and a just noticeable stimulation by $1/1700$ grain in 175 cc., while no result was obtained with $1/4000$ grain in 175 cc. The minimum physiol. dose of eserine, therefore, is $1/1700$ grain in 175 cc., which is approx. a 0.00001% soln., and corresponds to the 7th decimal diln.

JOSEPH S. HERBURN

Action of adrenaline, aromatic amines, and amino acids on skeletal muscle. KWANICHIRO OKUSHIMA. *Acta Schol. Med. Univ. Imperial Kioto* 3, 261-76 (1919).—Adrenaline increases the indirect irritability and the performance of the skeletal muscle so that the stimulation waves are frequently diminished, and the degree of contraction is not inconsiderably increased. Only slight concns. are required to produce these effects. With greater concns. the action is scarcely noticeable; and at still greater concns., the irritability is even lessened. The greater the concn., the more marked the phenomena of paralysis. None of these phenomena are noted on direct stimulation of curarized muscle. Therefore, the action is exerted on the app. of the motor nerve endings. If the concn. be increased up to a certain point, the indirect irritability of the muscle entirely disappears, while the muscle itself still responds to direct stimuli. Curari exerts an action antagonistic to that of adrenaline; and adrenaline can retard the paralyzing action of curari to a certain extent. In small doses, adrenaline can prevent more or less the paralyzing action of a large dose of nicotine. However, the paralysis, which is produced by a very large dose of adrenaline, is not stopped by a concn. of nicotine which by itself is sufficient to act as a stimulus. A mixt. of adrenaline and nicotine in their stimulating concns. acts like a highly concd. adrenaline soln., i. e., the action of the two compounds is additive under these conditions. The aromatic amines, tyramine and phenylethylamine, act on the app. of the motor nerve endings of the striated muscles, as stimulants in lower concns., and as paralyzers in higher concns. Amino acids are usually much less poisonous than the amines; yet several amino acids possess some activity. Glycocoll, alanine, leucine, and glutaminic acid act somewhat like the amines; glutaminic acid is most reactive; leucine and alanine are

somewhat less reactive; and glyccoll is least reactive. All these compds. exert a favorable, even though slight, action on the app. of the motor nerve endings, if applied in the proper concn.; in higher concns., they exert a slightly paralyzing action, while the muscle itself shows a much greater resistance. Asparagine has no particular action. Phenylalanine has a paralyzing action in higher concns., but never shows a stimulating action in any concn. Tyrosine is inactive on account of its slight soly.

JOSEPH S. HEFBURN

Antagonism between adrenaline and atropine in their action on organs composed of smooth muscle. AKIRA GÔHARA. *Acta Schol. Med. Univ. Imperial Kioto* 3, 362-75 (1920).—From expts. on rabbits, the following conclusions are drawn: The stimulation of the uterus, Fallopian tube, and spermatic cord and of the blood vessels, which is produced by adrenaline, is counteracted by atropine in a concn. which exerts a stimulating rather than a paralyzing action on the muscles. Therefore, atropine paralyzes not only the parasympathetic nerve elements, but also the sympathetic nerve elements which convey sensations. The inhibitory fibers are not affected by the paralyzing action of the atropine. The stimulation of the uterus and Fallopian tube, which is produced by atropine, is, in all probability, muscular, and is counteracted by adrenaline even in stimulating doses. The inhibitory impulse of the sympathetic system is able to suppress the muscular stimulation to a certain extent.

JOSEPH S. HEFBURN

Physiological experiments on poison gases. ALFRED N. RICHARDS. *Trans. Coll. Physicians, Philadelphia* (3) 41, 129-30 (1919).—A summary is given of the methods used for the detn. of the toxicity of poison gases under both lab. and field conditions. The mortality of animals which have been exposed to lethal gases of the Cl_2 and COCl_2 group is regularly lessened if they be subjected to bleeding soon after gassing. Clothing for protection against mustard gas is also considered.

JOSEPH S. HEFBURN

Action of adrenaline upon the heat regulation. SRIKO KONDO. *Acta Schol. Med. Univ. Imperial. Kioto* 3, 199-205 (1919).—Injections of adrenaline, either subcutaneous, intravenous, or intraperitoneal, in small doses produced scarcely any effect upon the temp.; its injection in larger amts. caused only a slight fall in temp. This temp. effect of adrenaline was not appreciably affected by the surroundings, sugar supply, or heat-stroke. An increase in temp. was almost invariably produced by intravenous administration of adrenaline, provided the exptl. animal had previously been given thyreoidine or peptone, and was occasionally produced by such administration of adrenaline after the use of atropine, or after section of the abdominal vagus nerve. Intracerebral injection of adrenaline in either a large or a small dose, immediately produced a marked rise in temp.; this phenomenon indicates that adrenaline acts upon the central nervous system; the effect of the adrenaline was counteracted by antipyrine, but not by morphine and pilocarpine; the rise in temp. was still marked in rabbits which had been starved for 6 days, and was but slight in rabbits which had been starved for 8 days; this action of adrenaline was slightly retarded by thyroidectomy. A very gradual rise in temp. was produced by intracerebral injection of NaCl soln. or of olive oil, or by subcutaneous administration of certain amts. of thyreoidine (desiccated thyroid gland), iodothylin, and peptone. NaI, glyccoll, asparagine, histamine, and tyramine apparently had no influence upon the temp. Iodival (monoiodoisovalerylurea) in large doses (0.25 g. per kg. of body wt., given subcutaneously) produced a distinct fall in temp. Iodipin (an addition compd. of I and sesame oil) produced a slight rise in temp. when injected subcutaneously in a dosage of 2 cc. per kg. of body wt. Subcutaneous administration of tyrosine (0.05 to 0.1 g. per kg. of body wt.) also caused a slight rise in temp.

JOSEPH S. HEFBURN

Action of vegetabilia cathartics and of bila on the uterus. S. OKAMOTO. *Kyoto Igaku Zasshi* 15, No. 3, 68-83 (1918); *Jap. Med. Literature* 5, 32 (1920).—The uterus of the rabbit was stimulated by administration of small and medium doses of the cathar-

tics, and was depressed by administration of large doses. Bile usually exerted a stimulating action in the rabbit and a depressing action in the rat. JOSEPH S. HEPBURN

Physiological effects of lime nitrogen. SEEBNER. *Chem.-Ztg.* 44, 369-70, 382-3 (1920).—Lime nitrogen (com. Ca cyanamide used as a fertilizer) has been claimed to produce injuries of the skin and of the respiratory tract, to act as a poison, and to cause a typical "lime nitrogen disease." The injuries to the skin are simply those produced by any dust containing free caustic CaO; they may be largely prevented by avoidance of the dust, personal cleanliness, and protection of the exposed skin by a coating of oil, fat, or vaseline. The injuries to the respiratory tract are the same as those caused by any dust; prophylaxis consists in prevention of the inhalation of the dust, *e. g.*, by use of a mask. Ca cyanamide is not a poison; it does not contain a preformed CN group; the lethal dose is 0.23 g. for the dog, 1.4 g. for the rabbit, and approx. 40 to 50 g. for man; this amt. must be ingested at one time; the effect is not cumulative; most other chem. fertilizers are lethal in smaller doses, and also exert a cumulative effect. The *lime nitrogen disease* consists essentially of a rush of blood to the head and upper part of the body, air-hunger, stimulation of the heart and acceleration of the pulse; and, in severe cases, vomiting and diarrhea. It occurs in individuals who ingest alcoholic liquors while exposed to cyanamide dust or shortly thereafter; the prophylaxis is to abstain from use of such liquors under the conditions stated. In a mild attack, merely a marked flushing of the face occurs. JOSEPH S. HEPBURN

Changes in peripheral nerves caused by local anesthetics. K. UYEDA. *Kyoto Igaku Zasshi* 15, No. 3, 127-52(1918); *Jap. Med. Literature* 5, 33(1920).—Study was made of the histological changes produced in hens by the perineural injection of cocaine, novocaine, tropacocaine, and allocaine S. Congestion of the vessels occurred, accompanied by infiltration of the walls of the veins with round cells, swelling and desquamation of the endothelial cells, and a swelling of the axis cylinders and medullary sheaths, which subsided after 6 to 12 hours. Novocaine produced the least marked changes. Cocaine produced the most marked change in the endothelial cells. J. S. H.

Cotton process ether for dental operations. JAMES COTTON. *Dental Cosmos* 63, 11-21(1921).—A discussion of the synergists required to be present in ether in order to obtain good analgesia and anesthesia, and of the mode of administration.

JOSEPH S. HEPBURN

Carbon monoxide poisoning from the use of petrol engines (LOGAN) 21. Formation of poisonous gases by certain forms of gas-fired water heaters (SCHUCH) 21.

I—ZOÖLOGY

R. A. GORTNER

Chemical study of an extract of eel. S. YOSHIMURA. *Taiwan Igakukai Zasshi* No. 184, 361-2(1918); *Jap. Med. Literature* 5, 29(1920).—The eel (*Pluturus fastians*, Dans) was sliced, and extd. with Et₂O for 3 or 4 days. This ext. was evapd. and treated with alc. KOH, then with water. A cryst. substance was obtained as colorless plates, neutral in reaction, m. 145°, insol. in H₂O, sol. in warm alc., Et₂O, and CHCl₃. The substance gave a red color, deepening on standing, with concd. H₂SO₄. When the soln. of the substance in CHCl₃ was treated with concd. H₂SO₄, the CHCl₃ layer became deep red, and the acid acquired a greenish yellow fluorescence; on evapn. to dryness in a porcelain vessel, the CHCl₃ layer became blue, then greenish yellow. The CHCl₃ soln. of the substance reacted with glacial AcOH and concd. H₂SO₄ to give a series of colors: red, blue, deep blue. [These reactions are similar to, but not identical with those of cholesterol.—ABSTR.] This eel is used as a tonic, and as a remedy for gonorrhea and for diseases of women. JOSEPH S. HEPBURN

Chemical study of several marine mollusks of the Pacific coast. P. GERHARD ALBRECHT. *Stanford Univ. J. Biol. Chem.* 45, 395-405(1921).—The organisms

studied were the *Abalone*, Pismo clam (*Tivella stultorum*), giant chiton (*Cryptochiton stelleri*), *Isnochiton* (*Isnochiton conspicuus*) and owl limpet (*Lottia gigantea*). The digestive juices of the stomach and intestines of each of these have a distinct acid reaction and contain a catalase, glycogenase, lactase, lipase, maltase, protease, invertase, urease, amylase, and emulsin, but no uricase nor cytase. The muscle tissue of each species was analyzed and the results are reported in detail. "Particularly notable among the results on this tissue are the relatively high protein content of *Abalone*, 23%; the low protein content of the Pismo clam, 10.26%; the large amt. of ash in all the forms; and especially in the limpet 7.54% and the Pismo clam 5.1% as against an av. of approx. 1% in the common mammalian muscle tissues used as food and 1 to 1.5% in the sea fishes; the presence of determinable amts. of urea in *Abalone*, Pismo clam, *Isnochiton* and limpet; the large amts. of reducing sugars yielded on hydrolysis of the EtOH extr. from 5.26 to 27.2% of the residue after removal of the EtOH; and finally the occurrence of creatinine and creatine in *Abalone*, here reported for the first time in molluscan tissue. Enzymes were found only in 3 cases: an amylase and glycogenase in *Cryptochiton* and a urease in the Pismo clam.

I. GREENWALD

Biological study of *Paragonimus westermanii*. T. YOKAGAWA. *Taiwan Igakukai Zasshi* No. 184, 311-54(1918); *Jap. Med. Literature* 5, 29-30(1920).—A study of the action of various solns. on the encysted cercariae of this parasite. In the living animal, ingested encysted forms are never released in the stomach, but only after entering the intestine; some are evacuated unchanged in the feces. JOS. S. HEPBURN

Development of *Ascaris*. T. YOSHIDA. *Tokyo Iji Shinji* No. 2066, 555-61(1918); *Jap. Med. Literature* 5, 43(1920).—The eggs of *Ascaris* developed in the following solns.: 0.7% HCl, 0.3% HNO₃, 4% AcOH, 1% NaOH, 0.7% HgCl₂, 7.5% NaCl, 5% chloride of lime, 5% formalin, 0.3% PhOH.

JOSEPH S. HEPBURN

An explanation for the variations in the intensity of oxidation in the life-cycle. W. E. BURGE AND E. L. BURGE. Univ. Ill. *J. Expt. Zoology* 32, 203-6(1921).—Various stages in the life-cycle of the Colorado potato beetle (*Lepinotarsa decemlineata*) were used in these expts. The intensity of oxidation was measured by the increase in catalase in the respective stages. The catalase content was detd. as the number of cc. of O₂ liberated by 0.5 g. of fresh, ground tissue when neutral H₂O₂ was added to it in an appropriate app. The results were as follows: unfertilized egg, 18 cc. O₂; fertilized egg, 35 cc.; newly hatched larva, 280 cc.; quarter grown larva, 800 cc.; half grown larva 1250 cc.; three-quarter grown larva, 1725 cc.; full grown larva, 1750 cc.; pupa, 1800 cc.; adult beetle, 1750 cc.; old beetle, 900 cc. Thus the low rate of oxidation in the unfertilized egg is due to its low catalase content. The increase of oxidation in the fertilized egg is brought about by the stimulation to an increased production of catalase by the spermatozoon. Similarly, in youth there is an increase in respiratory metabolism or oxidation, and in old age a decrease, attributed to the increase and decrease respectively, of the catalase in the tissues. The view is held that the spermatozoon furnishes a substance which stimulates the egg to an increased production of catalase.

CHAS. H. RICHARDSON

Some studies on the influence of environmental factors on the hatching of the eggs of *Aphis avenae* Fabricius and *Aphis pomi* DeGeer. ALVAN PETERSON. Rutgers Coll., N. J. *Ann. Entomol. Soc. Amer.* 13, 391-400(1921).—The factors in the natural environment which det. to a considerable extent the hatching ratio of aphids' eggs are moisture, temp. and wind velocity. Expts. and observations showed that the moisture content of the air largely det. the % of eggs which hatch and probably also the rate of splitting of the outside covering of the eggs. Low humidity hinders, high humidity favors these phenomena. cf. C. A. 14, 3494.

CHAS. H. RICHARDSON

12—FOODS

W. D. BIGELOW AND A. H. STEVENSON

Food supply of Philadelphia. SENECA EGBERT. *Trans. Coll. Physicians Philadelphia* [3] 41, 287-314 (1919).—Report of a survey. JOSEPH S. HEPBURN

The relationship between the hydrogen-ion concentration and the bacterial content of commercial milk. ERWIN W. SCHULTZ, ALBERTA MARK AND HAROLD J. BEAVER. *J. Dairy Sci.* 4, 1-6 (1921).—The bacterial content of milk from a city dairy for each p_H from 6.8 to 4.6 indicates that at 6.6 the count begins to run high, averaging 16,000,000 and at 6.5 reaching 100,000,000. Acidity cannot be tasted at these p_H readings, being first detected by taste at $p_H = 6.0$. A curve is given which when more fully fixed by further detns. will make it possible to estimate bacterial count from a detn. of p_H . The method of detg. p_H is described. H. A. LEPPER

Grading milk by the acid test; influence of acids in the ration on the acidity of milk. H. H. SOMMER AND E. B. HART. *J. Dairy Sci.* 4, 7-11 (1921).—Inorg. acids (H_2SO_4) in the ration do not affect the milk. Milk of high acidity is rejected by condenseries owing to its coagulation on sterilization. All milk with an apparent acidity over 0.18% is not undesirable. The present test does not measure objectionable acidity due to fermentation and does not differentiate between it and apparent acidity. Apparent acidity of milk from a farm should be detd. at intervals of several weeks and an increase 0.03% of should be allowed owing to slight fermentation for acceptable milk from that farm. H. A. LEPPER

The cryoscopy of milk. JULIUS HORTVER. *J. Ind. Eng. Chem.* 13, 198-208 (1921).—The f. ps. of blood and milk approach a physiol. const., viz. -0.550° to -0.560° . The advisability of using this const. in the detection of abnormal or watered milk is considered. If milk that has not soured is to be examd. full reliance can be placed on the f. p. test. Souring gives an abnormally low f. p., for which a correction deduced by Keister has been proposed, but because of insufficient data it is not recommended. The av. of 75 samples of known pure milk examd. by H. shows a max. f. p. of -0.534° , a min. of -0.562° and an av. of -0.548° . From either Winter's table or the formula $W = [100(T - T')/T]$, in which W is the % added water, T the f. p. of normal milk (-0.550) and T' the observed f. p., it is possible to det. the amt. of added water accurately. The results of refractometric and cryoscopic detns. upon milks of known water additions are reported by H. The simplification and standardization of the freezing-point apparatus for commercial analysis are discussed and an improved form for this purpose is described. H. F. ZOLLER

The estimation of butter fat in cream. HARRY B. SIEGMUND AND R. SEWELL CRAIG. *J. Dairy Sci.* 4, 32-8 (1921).—The Roesse-Gottlieb method does not give accurate results on some samples of cream because of partial churning taking place in shipment, causing a lack of uniformity in the sample. The Babcock method, owing to use of larger samples, minimizes this error, but as usually performed gives high results, probably due to occlusion of H_2O or acid in the fat column. Sufficient centrifugal force (1600 r. p. m.) overcomes this error. The latter method with sufficient centrifugizing is relieved the better in routine work. H. A. LEPPER

A comparative study of some methods for determining the fat content of skim milk. T. J. MCINERNEY AND H. C. TROY. N. Y. (Cornell) Agr. Expt. Sta., *Bull.* 401, 69-85 (1920).—The regular Babcock test gives low results, as compared with gravimetric methods, for the detn. of fat in skim milk. When the test was modified by increasing the amt. of acid used to 25-28 cc., and centrifuging at a higher temp. (at least $180^\circ F.$) with greater speed and for a longer time, results could then be obtained for the fat content of skim milk which compared favorably with those obtained by gravimetric methods. W. H. ROSS

Estimation of total solid substance in soy sauce by means of the specific gravity.

RINJIRO SEGAWA. *J. Pharm. Soc. (Japan)* No. 465, 940-73(1920).—The solid substance in soy sauce consists of about equal parts of org. and inorg. matter, each brand having characteristic variations both in the amt. and ratio of these substances. NaCl constitutes the major portion of the inorg. matters, varying from 25 to 40 g. per 100 cc. From the relationship between sp. gr. of NaCl and its concn. calcd. from Gerlach's data, it was found that in the range of concns. of NaCl occurring in the soy, sp. gr. of NaCl follows the formula $Y = 1.00021 + 0.0071X - 0.000026X^2$. From the sp. gr. of the soy, the amt. of mineral matter, and the amt. of NaCl and total solids in 100 cc. of the soys of various brands, it was shown that the relationship between the sp. gr. of the org. matter and its concn. can be expressed by $Y = 0.9997 + 0.00399X$, and from this is calcd. a complete table whereby concn. of the total org. matter can be read off from the sp. gr. of the org. matter. Extensive comparison between the total solids, actually weighed and the amt. calcd. from the sp. gr. shows, remarkable agreement. The routine method is as follows: 50 cc. of the soy is carefully made up to 100 cc. in a volumetric flask, and its sp. gr. is measured at 15°. The amt. of NaCl in 50 cc. is detd. by the $AgNO_3$ method, and the corresponding sp. gr. is found from the table. The sp. gr. of the org. matter is then calcd. from the following formula: sp. gr. of dil. soy—the sp. gr. of NaCl contained in 100 cc. of the dil. soy \div 1.0000 = sp. gr. of org. matter in the dil. 100 cc. of soy. From this sp. gr. the amt. of org. matter can be read off from the table. The sum of NaCl + org. matter multiplied by 2 expresses the total solids in 100 cc. of the original soy sauce. The calcd. tables showing the relation between the sp. gr. and concn. for NaCl and the org. matter are given.

S. T.

Soy bean problem. DOROTHY M. ADKINS. *Sci. Progress* 15, 445-51(1921).—The use of soy beans for human nutrition, as a stock food, and as a source of oil and fertilizer is discussed.

JOSEPH S. HEPBURN

(Canned salmon.) Report of Chemist; Natl. Cannery Assoc., Pacific Fisheries Investigations. R. W. CLOUGH. 2nd Ann. Report of Director of Investigations 1920, 3-6.—No skatole and only bare traces of indole were found in fresh or cold-storage salmon. Indole or a substance giving its reaction is formed by scorching fresh salmon or over-processing canned salmon, but in the latter case not in quantity sufficient to condemn the fish. The indole content increases regularly with the time the fish is kept under cannery conditions after being caught; 72-hr. fish showed excessive indole. Canning apparently did not change the indole content. The gills contained much indole after 24 hrs., increasing several hundred times in 6 days. The viscera showed practically none in 1 to 6 days. Indole was found in large quantities in limburger, Camembert and Camembert cheeses and canned shrimp. Its presence in canned salmon, over a minute quantity, shows that the fish was practically decompd. before canning. Not all salmon canned from decompd. fish shows indole. No data, tests nor expts. are given.

H. A. LEPPER

Storage of flavoring materials. MELVIN DEGROOTH. *Tea and Coffee Trade J.* 40, 346, 348(1921).—A practical discussion of various flavoring materials and their proper storage by ext. makers, indicating chem. reasons for deterioration, such as terebinthination of terpenes by O absorption, oxidation of aromatic aldehyde to inert acids, hydrolysis of aq. solns. of ester, etc.

C. W. TRIGG

The potability of lemon extracts. MELVIN DEGROOTH. *Spice Mill* 44, 502, 504(1921).—Rigid adherence to the federal standards prevents the abuse of lemon exts. for beverage purposes. Study of the compn. of lemon exts. manufd. 20 years ago shows a large excess of alc. in many cases and sometimes the complete absence of an appreciable amt. of oil of lemon. These products could be employed as a beverage without difficulty or harm.

C. W. TRIGG

The degree of sweetness of dulcin and saccharin. THEODOR PAUL. *Chem.-Zig.* 45, 38(1921).—The degree of sweetness of saccharin is unproportionally increased by the addition of dulcin. The addition of 120 mg. of dulcin to 280 mg. of saccharin in 1 liter increases the sweetness equal to a liter soln. contg. 535 mg. of saccharin. The taste of the mixed soln. is more pleasant than that of saccharin alone.

H. A. LEPPER

The investigation and valuation of artificial honey. GEORG BORRIES. *Arch. Reichsgesundh.* 52, 650-6(1920).—Artificial honey can be manufd. in solid form (Schnittfest). The effect of the sucrose, H_2O , and non-sugar solids on this property is discussed. The av. compn. of 10 artificial honeys was invert sugar 78.8, sucrose 4.5, total sugar 78.4, solids 82.0, non-sugar solids 3.6, and H_2O 18.0%. Accurate methods are given for detg. solids and sugars as well as for sampling, which are considered applicable also to real honey.

H. A. LEPPER

New applications of dill seed in food industry. R. COHN. *Pharm. Monatshefte* 1, 149(1920).—An address descriptive of expts. leading to the prepn. of "dill salt" ($NaCl$ impregnated with an alc. ext. of the seed), roasted seed (freed from essential oil) and the ext. therefrom for use as a *coffee substitute*, for tablets, pills, dragees, etc.

W. O. E.

Composition and preservation of foodstuffs. PAUL RAZOUS. *Industrie chimique* 7, 298-301, 342-3, 381-3(1920).—A general description of the chem. compn. of *meat*, of the various methods by which it can be preserved (antiseptics, cooking and sterilizing, refrigerating), of the effects of *refrigeration* on meat, and of the working of a properly organized abattoir; together with a general description of the compn. and preservation of *fish* by cold storage, and of the facilities provided (or to be provided) at Lorient (France) for the handling of fish.

A. P.-C.

Colloid problems in bread-making. R. WHYNER. *Third Rept. on Colloid Chemistry, Brit. Assoc.* 1920.—Discusses the starch, gluten, mineral salts and enzymes in flour; also yeast, water, salt, fat, milk, etc.

JEROME ALEXANDER

Amylase of *Rhizopus tritici* (HARTER) 11A. Composition of the sunflower and corn plants (SHAW, WRIGHT) 11D. Orange vinegar (BROOKS) 16. Crystalline sugar from honey (Jap. pat. 36,201) 28. Iodine compounds of fatty acids (Jap. pat. 36,182) 27.

Sterilizing milk or other liquids. O. LOBECK. U. S. 1,369,345, Feb. 22. Milk or other liquid to be sterilized is thinly distributed centrifugally and heated *in vacuo* to a temp. below its b. p.

13—GENERAL INDUSTRIAL CHEMISTRY AND CHEMICAL ENGINEERING

HARLAN S. MINER

Industrial and agricultural chemistry in the British West Indies, with some account of the work of Sir Francis Watts, Imperial Commissioner of Agriculture. C. A. BROWN. *J. Ind. Eng. Chem.* 13, 78-83(1921), illus.—Descriptive of the principal agricultural chem. enterprises, the products being cane sugar, cane sirup, cacao, citric acid, Ca citrate, essential oils, etc. Citric acid and its salts together with the *esselle* or distd. oil are entirely from limes. The process of manuf. of the Ca salt as devised by W. is given. The essential oils are those from the lime, bay oil, thymol. Rubber has not yet attained importance but much work is being done on it. Other minor products are starch, vegetable oils, tanning materials, dyewood, copra. The work of Dr. Watts is discussed.

P. D. V. MANNING

Recent state of the chemical industry in Japan. FUSAJIRO KODERA. *J. Chem. Ind. (Japan)* 23, 631-44(1920).—Presidential address. Various statistics of the chem. industry in Japan are given. During 1915-18, export of the chemical products gradually exceeded the import, the amt. of excess export reaching 150 millions of dollars for 1918. For the same year 192 new industrial enterprises were incorporated. Educational data show that 475 chemists were graduated from colleges and universities in 1918. Research activity is represented by original contribution of 138 chem. articles; there are now more than 24 research institutions. Patents obtained from the Japanese Government are tabulated for 1908-18; in 1918 there were 515, of which 17% were granted to foreigners. For the further development of chem. industry more fundamental research along pure chem. and physical sciences is urged. S. T.

Patent-protected products. E. FERTIG. *Z. angew. Chem.* 34, Aufsatzteil, 33-5 (1921).—A critical résumé of German patent law, with numerous citations, referring to products as distinguished from processes. The exceptional position of chem. inventions in the law of 1877 remains in effect now, the whole chem. industry having desired its retention. Patent rights in a process extend also to the products directly prepd. by it, and even to the sale, use and importation of such products. It is assumed, until proof to the contrary is offered, that every material of the same properties as the new substance has been made by the patented process. That the protection of a "direct product of a process" is not of equal value as that afforded by a patent of the product itself is not questioned. The holder of a patent on a process is not protected against a similar product made by a different process. While under "product patents" every method of production falls under the protection of the patent, the law makes exceptions for inventions of substances which are prepared by chem. processes. Moot points in patent law are discussed, and suggestions for its improvement are offered. W. C. E.

Industrial tuberculosis and the control of the factory dust problem. C. E. A. WINSLOW AND LEONARD GREENBURG. *J. Ind. Hyg.* 2, 333-43, 378-95(1921).—A critical study with bibliography. The first installment is devoted essentially to the relation between industrial dusts and respiratory disease. The second installment contains sections on: method of studying dust content of air, variations in dust content of air from normal and industrial environments, control of dust hazard (by substitution of wet for dry processes, by conduct of dust-producing operations in enclosed chambers, by operation of hoods and local exhaust ventilation, by wearing of respirators and helmets), importance of definite analytical standards in control of industrial dust hazards. JOSEPH S. HEPBURN

Occupation in relation to tuberculosis. GEORGE M. KOBER. *Trans. Coll. Physicians Philadelphia* [3] 41, 314-37(1919).—A discussion of the relationship between the occurrence of tuberculosis in various occupations and the dusts of these occupations, including dusts containing harmful chem. compds. JOSEPH S. HEPBURN

Catalysis in industrial chemistry. E. K. RIDEAL. *Chem. Age (London)* 4, 245-6 (1921); *Gas World* 74, 160(1921); *Gas J.* 153, 543-4(1921).—A discussion of industrial processes of catalytic oxidation. It is pointed out that catalytic oxidation processes can be divided into 3 classes: complete, fractional and selective. The 1st of these is exemplified in the heavy chem. industry by the contact process of H_2SO_4 manuf. and the oxidation of NH_3 to NO . The 2nd class is represented by the acceleration of the drying of oils by salts of the multivalent metals, by the catalytic oxidation by V_2O_5 of $C_{10}H_8$ to $C_6H_4(CO)_2O$ and of C_6H_6 to maleic anhydride, and the catalytic oxidation of the aliphatic hydrocarbons to fatty acids and alcs. with the simultaneous production of waxes. The development of catalytic processes in the gas industry, and the catalytic production of gaseous fuel also are considered. In conclusion, R. points out that at 550° to 650° decompn. of ring structures commences in the presence of catalysts,

C_2H_4 decomp. into C, H, and hydrocarbon chain residues, while at 600° to 700° the satd. hydrocarbons undergo thermal degradation, e. g., $C_2H_4 = C_2H_2 + H_2$ and $CH_4 = C + 2H_2$. The degradation of coal appears to take place in stages of this kind and in each stage a reversible reaction occurs. Equil. in the presence of only feebly catalytically active materials might not have time to be accomplished, with the result that the complex products in coal undergo complete destruction to H and CO with complete loss of intermediate products having not only higher calorific value as illuminants, but possessing potential value outside of that of carburizing agent for gaseous fuel.

H. JERMAIN CREIGHTON

Catalysis in industrial chemistry. Processes of hydrogenation. E. K. RIDGAL. *Gas J.* 153, 821-2(1921).—The recent growth in the demand for H in industry has stimulated research. Theoretically, it should be more economical to manuf. H than blue water gas, but this has not yet been achieved. The *Mond-Langer* catalytic process for mfg. H from water gas is past the exptl. stage and is in operation where large amts. of H are required and where small amts. of inerts are not objectionable. A catalyst, usually Fe_3O_4 mixed with suitable promoters such as Cr_2O_3 , is used to attain equil. at relatively high velocities and low temps. in the water gas reaction. Water gas mixed with steam is passed through the catalytic material at $550-600^\circ$. Then the steam is removed by condensation, the CO_2 by pressure scrubbing with water, and the 2% CO either by scrubbing with cuprous $(NH_4)_2CO_3$ soln. or by fractional combustion. A catalyst operative at 400° is urgently needed for this process. Also research should be made to produce water gas free from inerts. The *Bergius* process attempts to effect the water-gas production and reaction in 1 stage at 300° . Coke is heated with water to this temp. in autoclaves. The critical pressure of the water at this temp., 89 atm., must be maintained. TI salts are found to exert a markedly catalytic action. The primary action would also be accelerated by fine grading of the coke. A charge of 12 kg. of coke and 24 kg. of water should yield approx. 1600 cu. ft. of H. The autoclave would require a capacity of only 1.5 cu. ft. The ultimate solo. of manuf. of H from coke will probably be found in such a direct process. The utilization of H for mfg. hexahydrobenzene is also a possible development in the gas industry. R. theo considers hydrogenation of oils and fats with Ni as a catalyst, the synthesis of NH_3 by the Haber and the Claude processes, the sapon. of fats, the polymerization of isoprene to rubber, and the vulcanization of rubber goods.

J. L. WILEY

Chemical warfare as practiced by the Allies. ANDRÉ KLING. Municipal Lab. of Paris. *Rev. sci.* 58, 545-60(1920).—A general review of the chemicals used in warfare and the methods of employing them.

C. J. WEST

Oxygen and air respiratory devices. Gas masks. WILHELM HAASE-LAMPE. *Chem.-Ztg.* 45, 117-8(1921).—The gas mask is not to be considered as a substitute for O and air respiratory appliances. Before the World War efforts were made to develop gas helmets for use in mines, etc., each nation striving to perfect a "national" type. Now the aim is to perfect a standardized unit app., with a variety of fittings, that can become a "world type." Classifications of O and air helmets, gas masks and resuscitation devices (e. g., pulmotors), based upon their construction and uses, are presented. Cf. following abstr.

W. C. BRAUGH

Oxygen and air respiratory devices. Gas masks. WILHELM HAASE-LAMPE. *Chem.-Ztg.* 45, 142-6(1921); cf. preceding abstr.—Descriptions with diagrams of different types of app. (German). The following are included: *Portable breathing app. for O.*—Group 1a, injector app., Draeger type and Westphalia type. Each is made in 2 sizes, for 1 or 2 hrs. service and for helmet or mouth breathing. Group 1b, injectorless app.: (1) Draeger-Tueben for mouth breathing, $\frac{1}{2}$ hr. service; (2) navy respirator for mouth breathing, $\frac{1}{2}$ hr.; (3) army O protection app. (HSS-app.) for mouth

breathing, 1 hr.; (4) O protection app. (SS-app.) in 1, 2 and 3 hr. sizes for mouth breathing. This is the highest type of injectorless app.; (5) Magirus respirator with O attachment. This differs from all the above by having no caustic cartridge for removal of CO₂. Group 1c, app. using liquid air; (1) Aerolith, with mouth breathing for 2-hr. service; (2) Draegerolith for liquid O, 2-hr. service; heat for evapn. is furnished by air circulated by inflation and deflation of a bag during breathing. Group 1c, app. for generation of O, 1 hr. size with 1 proxylit cartridge and 2-hr. size with 2 cartridges. Group II, air-supplying app. (3 types): original Koenig, Magirus and Westphalia, all consist of helmets with tubes for supplying air from pumps. *Gas masks*.—The industrial gas protection app. is the forerunner of the German army gas mask. It consists of a tight-fitting leather mask, eye pieces with a gelatin layer inside to absorb moisture without losing transparency and a gas filter. The filter is a brass container whose absorbing material varies with the gas to be absorbed. *Oxygen resuscitation app.*: (1) App. for O inhalation; (2) pulmotor, (3) Inhabad resuscitator; (4) resuscitator of Dr. Bratt. The last three combine O inhalation with artificial respiration.

J. J. MORGAN

Practical points on erection and care of chemical stoneware apparatus. ISMAR GINSBERG. *Chem. Age* (N. Y.) 28, 252-3(1920).—A description of methods of erecting chem. stoneware app. in the plant and a discussion of points in their care, of compn. of cements, etc., illustrated with diagrams.

ISMAR GINSBERG

Treatise on distillation. THOS. H. DURRANS. *Perfumery and Essent. Oil Rec.* 11, 154-98(1920).—A valuable and comprehensive review, including mathematical treatment, of steam distn. The theoretical portion covers vapor pressure, relation between b. p. of different substances, correction of b. p. to normal pressure, distn. of unmiscible liquids, fractional steam distn., steam distn. under reduced or increased pressure, depression of vapor pressure of one substance by another, distn. of liquids miscible in all proportions, theory of fractional distn., sublimation. Then follows a practical section on the winning of essential oils by distn. with steam or water, a description of lab. app. and an appendix with useful tables of b. p. of many perfume chemicals and binary and ternary mixts. of these; also latent heats of vaporization, and yields of essential oils from various seeds, leaves, roots, etc. For high-temp. lab. baths tricresyl phosphate is recommended.

JEROME ALEXANDER

Steam in fractional distillation. RALPH SHAW. *Chem. Age* 3, 154(1920).—A brief description of current practice, especially of the fractionation and separation of various coal-tar and paraffin hydrocarbons.

JEROME ALEXANDER

Application of graphs to the study of commercial fractional distillation. MARCEL PONCHON. *Technique moderne* 13, 20-4, 55-8(1921).—Mathematical analysis of the process of fractional distn. Three fundamental graphs are required: (1) compn. of vapors from a liquid mixt. of variable compn.; (2) total heat of the liquid mixt. at its b. p.; (3) total heat of the vapor at the b. p. These curves can easily be prepd. in the lab., and require no complicated app. or manipulation, but are somewhat tedious to prepare. From them may be prepd. various simple graphs for the study of the operation and proper construction of the column. The results are not absolutely correct, because certain assumptions made in the development of the equations do not hold in practice; but corrections can be made which give very close approximations.

A. P.-C.

The driving of centrifuges. F. J. BROADBENT. *Chem. Age* (London) 4, 183-6 (1921).—According to prevailing English practice, the five methods used for driving centrifuges are: by direct steam, by steam turbine, by belt, by elec. motor and by water power. In the drive by direct steam a reciprocating engine is rigidly bolted to the outer casing, the connecting rod acting directly on the spindle. This type is suitable where there is a large supply of low-pressure steam. For the basket, the suspended

type of hydro-extractor must be used and the inlet and exhaust pipes of the engine should be flexible. An out-of-balance load is one disadvantage. The cost for coal with 40 lb. steam and starting 5 times per hour with coal at 50s. per ton, should not run over 4.5d. per hour. Because of its excessive steam cost, the turbine drive is used only in cases which require the use of exhaust steam in the basket, such as in the recovery of grease from oily waste. In the small high-speed machines, this type of drive is very economical, requiring but little power, and having the advantages of great simplicity, const. turning movement and no out-of-balance load. With outside belt drives, ball bearings can be used, but speed regulation is more difficult and slippage at starting gives trouble. In direct elec. drive, a slipping clutch is necessary because of the low efficiency of a. c. motors at low speeds. The design of this clutch depends upon the type of motor and current to be used, curves being given for this as well as a detailed discussion. According to B., with a battery of machines and especially in chem. works, water drive is best, it being characterized by simplicity, absence of clutch slippage and being applicable to any type of machine.

P. D. V. MANNING

Dilution of crank-case oil. W. F. PARISH. *J. Soc. Auto. Eng.* 8, 231-7(1921).—It is estimated that about 85% of engine service jobs have been caused by lack of lubrication due to dilution problems. Tests on a number of different lubricating oils showed a low fuel consumption during the first portion of the run with a rapid rise during the first hour. There is also a rise in fuel consumption after the sixth hour, caused by a gradual thickening of the oil due to carbon and metal deposits. This oil may be reclaimed by putting it, with H_2O , into steam-jacketed tanks, blowing in steam and sprinkling soda ash over the surface of the oil to form an emulsion and ppt. the foreign matter. The recovery is as high as 85%.

R. L. SIBLEY

Molded insulating compositions. R. T. FLEMING. *J. Inst. Elec. Eng.* (London) 57, 322-7(1920).—This paper gives a general outline of the properties of the raw materials and the methods of manufg. and testing the molded objects. Important raw materials are asbestos, shellac, rubber, and bakelite. Ceramic materials are not discussed.

D. MACRAE

Imbibition of gels (WILSON) 2.

CALENDAR, H. L.: Properties of Steam and Thermodynamic Theory of Turbines. New York: Longmans, Green & Co. 531 pp. \$14.

Lubricating mixture. L. B. LOCKHART. U. S. 1,369,678, Feb. 22. A mixt. adapted for use in internal-combustion engines is formed of oils of different degrees of viscosity and volatility such as mineral oil of 600-1200 viscosity (Saybolt) mixed with headlight oil, kerosene or sperm oil 4-6%.

Lubricating and cleaning oil. J. E. STRATER. U. S. 1,369,492, Feb. 22. A mixt. adapted for lubricating and cleaning leaf springs or machine bearings is formed of turpentine 50 gals., lubricating oil 50 gals., creosote oil 50 gals., ether 5 lbs. and powdered graphite 28 lbs.

14—WATER, SEWAGE AND SANITATION

EDWARD BARTOW

The determination of hydrogen sulfide in waters containing sulfides of calcium; sensitiveness of the reaction between starch and iodine. E. CHRÉTIEN AND H. VANDENBERGHE. *Ann. chim. anal. chim. appl.* 13, 19-23(1921).—If the alkalinity of the water is normal, the sulfide can be detd. directly by the iodometric method, but if it is

strongly alk., possibly owing to hydrolysis of Na_2SiO_3 . I_2 will react with OH^- to form hypiodite. It is then necessary to ppt. silicate and carbonate by means of Ba^{++} . The following procedure has been found to give good results: (1) To 1 liter of the water add 20 cc. of satd. BaCl_2 and filter. (2) By a preliminary test, find approx. how much of the water is required to decolorize 5 cc. of 0.01 N I_2 soln. If this should be about 280 cc., use 510 cc. of the silicate-free water (500 cc. of the original sample) and 10 cc. of 0.01 I_2 soln. (3) Into a large flask, add 10 cc. of 0.01 N I_2 , 0.1 g. of pure KI , and 510 cc. of the water. Shake well, add exactly 10 cc. of 0.01 N $\text{Na}_2\text{S}_2\text{O}_3$, 1 cc. of starch paste and titrate with the standard I_2 . (4) Carry out a blank in exactly the same manner but using 510 cc. of distilled water which is free from ammonia and nitrous acid. If the titration takes place at a temp. below 10° , in the presence of 0.1 g. of KI , as little as 0.15 cc. of 0.01 N I_2 soln. suffices to give a blue color with starch.

W. T. H.

Notes on the analysis of mineral sulfide water. J. G. FAIRCHILD. U. S. Geol. Survey. *J. Wash. Acad. Sci.* 10, 559-65(1920).—A method was needed for detecting and estg. not only the total sulfide S , but also the CO_2 as half bound and wholly bound. A series of synthetic waters was prepd. approximating the compn. of the mineral water from Texas under examn., the ratio of total S to total CO_2 being 1.4:1.0. After various expts., which are described, the following method was worked out: (1) The sample is boiled in a current of pure H_2 for 5 min., the evolved H_2S and half-bound CO_2 being collected in an ammoniacal soln. of CdCl_2 and BaCl_2 . (2) Acetic acid is added to the absorbing soln. and liberates the CO_2 but not the H_2S , detns. being made in the usual ways. The rate of boiling and passing H_2 , the presence or absence of Mg , and other factors introduce variations, so standard conditions must be obtained, by preliminary studies of synthetic waters. Data on the "alkalinity" of the water studied, the "acidity" of Ca and MgCl_2 toward alkali sulfides, and the production of H_2S from CaSO_4 by "org. matter" are also given.

E. T. WHERRY

The content of active carbonic acid in drinking water. T. M. KOLTHOFF. *Chem. Weekblad* 17, 558(1920); cf. *C. A.* 14, 3488; 15, 284.—K. replies to criticisms made in regard to the applicability of his theoretical deductions when the water contains much Mg . In that case the tables can also be used. Confirmatory results were obtained by Noll, who found that in the presence of Fe a correction must be applied to the titration of combined CO_2 and also for the derived quantity of active CO_2 calcd. from the tables of Tillmans and Heublein. The estd. amt. of active CO_2 agrees fairly well with the amt. given in Kolthoff's tables.

J. B. KRAK

Ground waters in the Norwalk, Suffield and Glastonbury areas, Conn. HAROLD S. PALMER. U. S. Geol. Survey. *Water-Supply Paper* 470, 166 pp., plates 12(1920).—The geographic and geologic features are described, also various methods of recovery of ground water and its use for public supplies. Analyses of 67 samples are grouped according to the different water-bearing formations and the constituents of each formation are averaged. The total solids range from 100 to 260 p. p. m., av. 143. The waters are classified as Ca , Na , carbonate, sulfate, or chloride according to the predominating constituent.

L. W. RIGGS

The purification of water for industrial uses. NOEL ADAM. *Publications techniques* 3, 7-9(June, July, Aug. 1920).—A. describes in detail the Gail and Adam app. for the continuous treatment of water (CaO and Na_2CO_3 being taken for the particular case described) for industrial purposes and its method of operation, together with examples of the nature and quantity of purifying reagents required for the treatment of various industrial waters; (waste liquors from bleacheries, straw pulp mills, starch factories, dairies, forges, pyroligneous acid plants, dyeworks, etc.)

A. P.-C.

Use of chlorine gas in water sterilization for British army. ANON. *Times Eng. Supp.*, Dec. 1920, *Eng. Contr.* 55, 331(1921).—Bleaching powder was first used, to

sterilize water coagulated and filtered in the field. Plants were rigged on 3-ton lorries to handle 400 gal. per hour. The use of liquid Cl followed by SO_2 gas to remove taste has been adapted to portable plants on motor trucks or barges and stationary plants.

LANGDON PEARSE

Sanitary control of a public swimming pool. GEORGE W. SIMONS, JR. *Am. J. Public Health* 11, 234-8(1921).—A combination of means was employed, (a) construction to control the movements of patrons, (b) periodic cleaning of the pool, (c) careful laundering of suits and towels and (d) strict regulations. G. C. BAKER

Lactose broth for isolating *Bacterium coli* from water. ESTHER A. WAGNER and W. F. MONFORT. *Am. J. Public Health* 11, 203-8(1921).—The authors suggest simplification of the technic by reducing the lactose content to 0.2% by the addition of gentian violet (0.001 to 0.00033%), also pasteurization in place of autoclaving to reduce the hydrolysis of the sugar. Beef extract may be eliminated if sufficient peptone is substituted. Clearer plates and readier identification of colonies is claimed. Gentian violet also ensures the keeping qualities of the broth. G. C. BAKER

Industrial wastes in relation to water supplies. W. DONALDSON. *Am. J. Public Health* 11, 193-8(1921).—See C. A. 14, 3734. G. C. BAKER

New water-purification plant at Hartshorne, Oklahoma. V. V. LONG. *Munic. County. Eng.* 60, 123-4(1921).—Two cities with a population of 7,500, handling water from a storage reservoir, are improving the water supply by aeration to remove odors, followed by coagulation (2-1/4 hr.) and 2 filter units. The plant handles 500,000 gal. per 24 hr., using 2 grains per gal. of $\text{Al}_2(\text{SO}_4)_3$. LANGDON PEARSE

Interpretation of the analytical results of experiments to determine the efficiency of installations for the purification of sewage. G. ROMIJN. *Water Bodem Lucht* 10, 40(1920). The state of oxidation of the nitrogenous substances as a measure of the degree of purification of purified sewage. G. ROMIJN. *Wasser und Gas* 11, Heft 1, Spalte 10-4(1920); through *Chem. Weekblad* 18, 39.—These two papers contain about the same material; the Dutch article, however, is somewhat more complete than the German one. The process of purifying polluted water is essentially a matter of "mineralizing" the organic materials present. R. discusses in detail the various chemical reactions representing the oxidation and reduction of nitrogenous compounds and shows that the O requirement varies with the particular kind of reaction which has taken place. L. H. ADAMS

Conservation of nitrogen with special reference to activated sludge. G. J. FOWLER. *J. Indian Inst. Science* 3, Part VII, 227-79; *Eng. Contr.* 55, 301-2(1921).—F. discusses the general problem of N plant food, and indicates lines of investigation needed, with lab. field and technical expts. The availability of N in sludge must be tried. The use of moderate heat is suggested for dewatering activated sludge. LANGDON PEARSE

Disposal of sludge on land as fertilizer. J. E. FARMER. *The Surveyor*, Dec. 17, 1920; *Eng. Contr.* 55, 298(1921). LANGDON PEARSE

Treatment of trade wastes by activated sludge process. W. H. MAKEPEACE. *Mun. Eng. San. Record*, Nov. 25, 1920; *Eng. Contr.* 55, 324(1921).—See C. A. 15, 914. LANGDON PEARSE

Municipal wastes: their character, collection and disposal. H. R. CROHURST. *U. S. Public Health Bull.* No. 107, 98 pp.(1920); cf. C. A. 15, 564, 913.—Municipal waste may be divided into sewage, garbage, rubbish, ashes, street sweepings, stable manure, excreta, and dead animals. The amt. and compn. of the various wastes are dependent upon the character of the population, the geographical and climatic location, and the seasonal changes. The collection of wastes offers no serious difficulties, but requires a careful study and adjustment of details which will vary in different localities. If all the refuse is mixed as collected the disposal is limited to dumping

into water, if a large vol. is available, or on land as a fill. In some cases mixed refuse is incinerated but it is not economical to pass ashes through an incinerator. If the garbage is sepd. from the ashes and rubbish, reduction is available as a means of garbage disposal with the recovery of grease, tankage and volatile gases, or it may be fed to animals. Both methods yield some revenue under proper supervision. Garbage may be buried, but gives no returns save the enrichment of the land. Ashes and rubbish are usually disposed of by filling low areas. If the ashes are sepd. from the garbage and rubbish, incineration is usually adopted for the combined wastes and the ashes are used for fills. Where the wastes are all sepd. garbage can be reduced, fed to hogs or buried. Ashes are removed for fills and the rubbish is disposed of in fills or sorted for salable material and the remainder burned. Street sweepings may be used for fills but disagreeable conditions arise from the dust in the vicinity of the dumping. Stable manure is utilized as a fertilizer but a systematic municipal collection is advised. Excreta should be disposed of by dumping into sewer systems, burial on land, or incineration. Private rendering companies, in addition to the municipal collection, utilize dead animals. Statistics, diagrams of incinerators, municipal powers as to garbage and a bibliography of refuse disposal are given.

G. C. BAKER

Investigation of dust in the air of granite-working plants. S. H. KATZ. *Bur. Mines, Repts. of Investigations No. 2213*, 2 pp. (1921).—In the pulmonary disease, designated as granite pneumoconiosis, to which granite cutters are subject it is estd. that particles of the hard insol. rock-forming materials about 1 micron in diam., are most injurious. Smaller particles either do not readily lodge or are more easily eliminated. In an investigation of this disease at Barre, Vermont, the principal granite-producing town of America, the dustiness of the air was detd. by 3 methods. Two of these methods involved the catching upon a sticky glass plate the dust particles from a vol. of air impinged at high velocity on the plate by a small air pump, the particles caught being counted by the aid of a powerful microscope. In the other method the air was filtered through a layer of granulated sugar, the sugar dissolved in H_2O , a portion examined microscopically to count the stone particles, then the whole sample filtered, the filter paper ignited and the dust weighed. The dustiness is expressed in millions of particles per cu. ft. and on a wt. basis in mg. per cu. ft.

G. W. STRATTON

Industrial tuberculosis and the control of the factory dust problem (WINSLOW GREENBURG) 13. Estimation of toxic water-soluble dust (ISZARD) 1. Sulfur bacteria (MARCKS) 11C. Bile powder in culture media for the demonstration of typhoid bacilli in water (TOYODA) 11C.

PARK, WILLIAM HALLOCK: *Public Health and Hygiene*. In contributions by eminent authorities. Philadelphia: Lea & Febiger. 884 pp. For review see *Am. J. Med. Sci.* 161, 279 (1921).

15—SOILS, FERTILIZERS AND AGRICULTURAL POISONS

J. J. SKINNER

New methods for the determination of potassium and ammonium. O. ARRHENIUS. *Medd. K. Vetenskapsakad. Nobelinst.* 4, No. 6, 1-5 (1920).—For soil analysis, the following procedures are recommended: To 15 cc. of soln. freed from all cations except Na and K, add 5 cc. of glacial AcOH and treat at about 0° with 5 cc. of $Na_2Co(NO_2)_6$, freshly prepd. according to Billmann. Allow to settle for 12 hr., decant off most of the liquid and centrifuge in a tube with capillary stem until the height of ppt. in the capillary becomes constant. By means of a scale on a mirror, estimate the K content from the height of ppt. For the detn. of N in soils present as

NH_3 or NH_4 salt, place 0.5 g. of Na_2SO_4 in a test-tube and dissolve in about 2 cc. of hot water. Add a weighed sample of soil (about 250 mg.) and shake well. Introduce 1' or 2 cc. of satd. NaOH soln. and a little light paraffin oil. Quickly insert a stopper which is fitted with suitable glass tubing and pass air through the soln. and thence into a measured vol. of standard HCl . Gradually increase the speed of the air stream and continue it for 15 or 20 min. Titrate the excess acid with standard alkali using methyl red as indicator. From the results obtained it appears that the soil certainly does not retain over 1 mg. of NH_3 and that this modified method of Folin is well adapted to soil analysis.

W. T. H.

A study in soil sampling. WILLIAM FREAR AND E. S. ERB. Penn. Agr. Expt. Sta. *J. Assoc. Off. Agr. Chem.* 4, 98-103(1920).—The bearing which the manner of collecting and sampling soil samples has upon the values obtained in their chem. analysis is illustrated by the results obtained in the mechanical and chem. analysis of different sets of samples.

W. H. Ross

Excavation method for determining the apparent specific gravity of soils. WILLIAM FREAR. Penn. Agr. Expt. Sta. *J. Assoc. Off. Agr. Chem.* 4, 103-5(1920).—Detailed directions are given for detg. the apparent sp. gr. of a soil by a new method, which differs in principle from the methods commonly used. In applying the method the soil is broken and removed from a roughly measured space and weighed before and after air-drying. The vol. of space from which the soil has been removed is measured by careful detn. of the vol. of dry sand required to fill it. From the data for soil weight and excavation vol., with any necessary correction for change in the vol. of the sand resulting from its transfer from the graduate to the excavation, the apparent sp. gr. can be computed.

W. H. Ross

Testing soils for acidity. EMIL TRUOG. Wis. Agr. Expt. Sta., *Bull.* 312, 1-24 (1920).—A detailed description of the Truog method (*C. A.* 10, 80) of testing soils for acidity together with a discussion on the relation of degree of acidity to the lime requirement of the soil.

W. H. Ross

Report on the lime requirement of soils. W. H. MACINTIRE. Tenn. Agr. Expt. Sta. *J. Assoc. Off. Agr. Chem.* 4, 108-23(1920).—This report gives results obtained in an individual rather than a comparative study of 8 different types of procedures for detg. the lime requirements of soils. The tests were made upon 10 different soils and the plan adopted was as follows: The lime requirement indication for each soil was detd. and the amt. of CaCO_3 so indicated was applied in the form of CO_2 -treated pptd. carbonate. The applications were made to the air-dry soil and thoroughly mixed, after which the soils were placed in stoppered bottles and wetted to a good condition. After about 48 hrs. contact, one set was permitted to dry spontaneously. A second set was kept under anaerobic condition for 2 weeks while a third set was kept for a month or more. The dried soils were again thoroughly mixed and the lime requirements obtained. It is suggested that the term "lime absorption coeff." be substituted for "lime requirement," and the belief is expressed that the Jones method offers the greatest possibilities for obtaining the coeff. of lime absorption.

W. H. Ross

Nitrogen and nutrition. E. LASSWITZ. *Schweiz. Chem.-Ztg.* 1920, 593-5.—Of the total N requirement of Germany, 80% is for agricultural purposes, and but 20% for the industries. Six crops (rye, wheat, summer barley, oats, potatoes, and meadow hay) require $1\frac{1}{2}$ million tons of N yearly. In the Haber process for the fixation of atm. N as developed by Bosch Os and U have been replaced by especially prepd. Fe "in the presence of certain substances" as a catalyst. A mixt. of steam and water gas is passed over a catalyst at a temp. of 400° to 500°; and a mixt. of H_2 and CO_2 is thus obtained containing only 1 to 2% of CO. Coke generator gas, containing N_2 and CO, now is admixed in such a proportion that the final gaseous mixt. contains N_2 and H_2 in the ratio 1:3. The CO_2 is removed by washing with water at a pressure

of 25 atm., the CO by washing with a cuprous soln. at a pressure of 200 atm. "The actual ammonia-process occurs in cycles spontaneously, since the NH_3 formed is removed, and fresh gas introduced. The end product is a 25% soln. of NH_3 in water." By treatment of gypsum with NH_3 and CO_2 , $(\text{NH}_4)_2\text{SO}_4$ is produced. By a process, which is not described, urea is prepd. on a large scale, by direct synthesis from NH_3 and CO_2 .

JOSEPH S. HERRBURN

The valuation of basic slag. JOHN HUGHES. *Chem. Trade J.* 68, 201-2(1921).—Lab. expts. show that the soly. and, presumably, the probable fertilizing value of slags depend upon the chem. compn. rather than upon specially fine grinding. 2% citric acid appears far too strong for detn. of the fertilizing value of basic slag. Expts. on 6 slags show enormous variation of P_2O_5 sol. in 2% acid, ranging from 29.77 to 95.68% of the total P_2O_5 . CaO no doubt contributes greatly to the beneficial effect which basic slag produces on soils deficient in CaO, since it constitutes the larger proportion of basic slag.

ALBERT R. MGRZ

The reactions taking place in Cyanamid when used in mixed fertilizers. W. S. LANDIS. American Cyanamid Co., N. Y. *Am. Fertilizer* 54, 49-55(1921).—The changes which take place in Cyanamid are reviewed and discussed with a view to showing the great reactivity of this material with practically all fertilizer materials, and the widely divergent character of the reaction products. When mixed with acid phosphate, K_2O salts, NaNO_3 and $(\text{NH}_4)_2\text{SO}_4$ in amts. not exceeding 60 lbs. to the ton, Cyanamid is converted mainly to urea and in a lesser degree to guanilyurea. It is possible that when proper precautions have not been taken in mixing a small amt. of dicyanodiamide may be found in the fertilizer just after mixing but this disappears in a few weeks. Cyanamid also reacts with the amino acids found in the ordinary ammoniated base goods to form complex org. acids, many of which have been identified and proved to be of excellent agricultural value. The reactions of Cyanamid are influenced to a marked degree by the character of the mixt., the temp. and the time. It is held that conclusions as to reaction products in comm. fertilizers must, therefore, be based only on mixts. prepd. on a large scale and in the same manner as practiced in standard mixing plants, and that the observations made by Harger (*C. A.* 15, 287) on the formation of dicyanodiamide from Cyanamid in mixts. prepd. in the lab. furnish no basis for conclusions as to the ultimate Cyanamid reactions in a mixed fertilizer. A criticism is also made of the Harger method (*C. A.* 15, 286) for detg. dicyanodiamide.

W. H. ROSS

Changes in Cyanamid when mixed with fertilizer materials. E. J. FRANKEL. American Cyanamid Co., N. Y. *Chem. Met. Eng.* 23, 1102(1920); cf. preceding abstr.—Dicyanodiamide cannot be produced in the presence of the ammoniated base compds. which form the bulk of the mixed fertilizer tonnage, and the transformation of Cyanamid into dicyanodiamide as observed by Harger (*C. A.* 15, 287) in lab. expts. with fertilizer materials does not take place in proper mixts. of the ordinary comm. fertilizers. In the ordinary acid phosphate mixt. it can be produced only in extremely small quantity by a direct violation of the prescribed rules for mixing and even then it rapidly disappears by conversion into more complex compds. of good fertilizer value.

W. H. ROSS

Nicotine sulfate in a dust carrier against truck-crop insects. ROY E. CAMPBELL. Bur. Entomology, U. S. Dept. Agric., *Circ.* 154, 1-15(1921).—Nicotine sulfate dust prepd. by incorporating 40% nicotine sulfate in a carrier of kaolin or of kaolin and lime proved superior to spraying for melon and cabbage aphids, onion thrips, cucumber beetles and some other insects, giving usually a better killing at a smaller cost and with a greater speed and ease of application. The dust may be combined with Pb arsenate or S for different types of insects, or for insects and fungous diseases.

W. H. ROSS

Report on insecticides and fungicides. O. B. WINTER. Mich. Agr. Expt. Sta. *J. Assoc. Off. Agr. Chem.* 4, 134-47(1920).—The cooperative work described in this report included a study of the detn. of Pb, Cu and Zn in such products as Bordeaux-lead arsenate, Bordeaux-zinc arsenite, etc.; and a comparison of the Gyory bromate method with the official I method for detg. As when present in HCl soln. The results obtained were promising and further work on the methods is recommended. Good results were also obtained with the distn. method of detg. total As in London purple when the coloring matter was first destroyed by heating the sample with a mixt. of ZnO and Na₂CO₃. From a study that was made of the I titration method for the analysis of straight lime-sulfur solns. it is concluded that this method agrees very closely with the ZnCl₂ method and is more practical for comm. analysis. It is, therefore, recommended that the detns. for total S and total CaO, which are practically the same for the 2 methods, be made official, and that the methods for detg. monosulfide equiv., thiosulfate S, sulfide S and sulfate S by the I titration method be made tentative.

W. H. ROSS

The influence of leaf hopper control on potato yields. J. R. EYER. State Coll., Pa. *J. Econ. Entomology* 14, 69-71(1921).—Standard Bordeaux mixt. was almost as effective as a Bordeaux-nicotine combination. The extra expense of the added nicotine was not compensated for by the slight increase in yield.

C. H. R.

Leconte's sawfly, an enemy of young pines. W. MIDDLETON. Bur. Entomology. *J. Agr. Res.* 20, 741-60(1921).—This paper is largely entomological. In large areas control cannot be practical because of the expense. In nurseries and parks a spray using 2 lbs. of powdered Pb arsenate per 50 gals. of H₂O should be used against the young larvae. Nicotine sulfate is a fairly satisfactory spray but the Pb arsenate spray is superior and does not injure the trees.

F. C. COOK

Action of chloropicrin on the germinating power of seeds. E. MIEGE. *Compt. rend.* 172, 170-3(1921).—Expts. were made by exposing wheat, rice, hemp, beet, flax and several legume seeds to the action of chloropicrin in various concns. for varying periods of time. The results proved that the destruction of insects usually found in seeds was efficient when chloropicrin in concns. of 15 to 20 cc. per cu. m. of space, was allowed to act 24 hrs. Higher concns. or longer contact were unnecessary. Flax and legume seeds lost none of their germinative power under this treatment, or with concns. up to 50 cc. per cu. m. The other seeds above mentioned lost on the average 30 to 40% in germinative power when exposed to 15 cc. chloropicrin per cu. m. for 24 hrs.

L. W. RIGGS

Experiments with grasshopper baits. J. R. PARKER AND H. L. SEAMANS. Montana State Coll. *J. Econ. Entomology* 14, 138-41(1921).—Amyl acetate was the best of a number of substances used to improve the attractiveness of poison bran mash for the grasshopper, *Camnula pellucida*. This result was obtained in the lab. and in the field on a large scale during a severe grasshopper infestation. Ext. of vanilla ranked second in attractiveness and was superior to any of the fresh fruits used. Of the latter, watermelon proved best, but the baits containing it were only a little more attractive than when NaCl alone was added. NaCl gave as good results as a combination of molasses and NaCl, and both of these combinations were better than oranges or lemons. Oranges ranked 5th in attractiveness, lemons 9th, and lemon extract, the least attractive substance tested, 10th. Cf. C. A. 13, 1512, 2954; 14, 3747.

CHAS. H. RICHARDSON

Industrial and agricultural chemistry in the British West Indies (BROWNE) 13. Physiological effects of lime-nitrogen (SIEBNER) 11H. Disposal of sludge on land as fertilizer (FARMER) 14. Conservation of nitrogen with special reference to activated

sludge (FOWLER) 14. A modified hydrogen electrode (HUDIG, STURM) 2. Determination of hydrogen-ion concentration (VAN ALSTINE) 7. Compound of urea with calcium nitrate (U. S. pat. 1,369,383) 18.

16—THE FERMENTATION INDUSTRIES

H. S. PAINE

Studies in the fermentation of cellulose. GILBERT J. FOWLER. *J. Indian Inst. Science* 3, Part IV, 39-60(1920).—Small quantities of Pb, Cu, and Zn salts stop fermentation, while acidity beyond 1% has a retarding influence. The rate of fermentation is at a max. (a) with a certain ratio of cellulose material and the inoculant, (b) at an optimum temp. (35°), (c) if the products are effectively removed from time to time. By gradually building up the bacterial emulsion (sludge from a septic tank) it is possible to obtain a daily vol. of gas equal to 80% of the vol. of space occupied by the fermenting material. The gaseous products contain 85% CH₄. Hemicelluloses give AcOH as the only sol. product. Butyric acid has not been detected. F. suggests the fermentation of waste cellulose materials for the production of power gas and AcOH.

G. C. BAKER

Notes on the discontinuous rectification of alcohol. E. CHENARD. *Chimie & industrie* 5, 27-8(1921).—The latent heat of vaporization of mixts. of alc. and water can be detd. by data obtained during the operation of a rectifying column. No actual data are given.

L. E. GILSON

Manufacture of ethyl alcohol from wood waste. E. C. SHERRARD. U. S. Forest Service, Madison, Wis. *Chem. Age* (N. Y.) 29, 76-9(1921).—Sawdust and other mill-waste from soft woods may profitably be converted into EtOH in locations where the supply of waste is uniform and const. for a period of 20 yrs. or more, and where there is a good supply of water and a fairly close source of H₂SO₄ and lime. Assuming a yield of 20 gal. of EtOH per ton of wood, as obtained by two plants in operation, the cost of 95% EtOH in a plant of 3600 gal. daily capacity is estd. at 0.247 per gal. Complete figures are given based on continuous operation using 180 tons of dry wood per day. A minimum production of 1500 gal. is necessary for successful operation. The process consists of the digestion of the shredded waste with dil. H₂SO₄ at 115-120 lbs., converting 20-25% of the dry wood into sugars. These are leached out, neutralized with milk of lime, fermented 96 hours and distd. with standard equipment.

A. R. LAMB

When is increased distillation from corn economical? LUDER. *Z. Spiritusind.* 44, 47-8(1921).—If increased utilization of corn by a distillery can only be realized by raising the gravity of the mash above 18° Balling, shortening the time of fermentation below 72 hours or overfilling the vats, the decreased yields which result will offset gains due to reduction of overhead expense.

W. B. V.

The operation of distilling apparatus in working up ripe corn mashes. LUDER. *Z. Spiritusind.* 44, 40(1921).—Hints as to the production of alc.-free slops and the operation of continuous stills.

W. B. V.

The utilization of the German potato crop during the milk, fat and meat shortage. C. HENNIG. *Z. Spiritusind.* 44, 24-5, 32-3, 41, 48-9(1921).—An extensive résumé of the arguments for unrestricted use of potatoes in the distilleries, with utilization of the slops as feeding-stuffs for domestic animals.

W. B. V.

Orange vinegar. R. O. BROOKS. *Spice Mill* 44, 492, 494(1921).—B. discusses briefly the article by Poore (*C. A.* 15, 402).

C. W. TRIGG

German pharmacopeia test for denatured brandy. F. ESCHBAUM. *Pharm. Ztg.* 66, 17-8(1921).—Directions are given for applying the test (violet color with Na nitro-

prusside) in the case of spirit, colorless alc. preps., colored liquids, and those containing S and I. W. O. E.

Detection of methanol in brandy. F. RABE. *Pharm. Ztg.* 66, 72(1921).—Attention is called to the fact that the Fendler and Mannich test with morphine-sulfuric acid is of positive value only in the event that this reagent is free from HCl, a condition obtainable by allowing it to stand $\frac{1}{2}$ hr. before use, after being freshly prepd. A control test with resorcinol-sulfuric acid is recommended. W. O. E.

Detection of methanol in brandy. G. MAUR. *Pharm. Ztg.* 66, 114-5(1921).—Comments on Rabe's article (cf. preceding abstr.). W. O. E.

Compressed yeast as a sugar by-product (ARNSTEN) 28. Alcohol from coke-oven gas (TIDMAN) 21. The solubility, rate of absorption and of evolution of gases, as influenced by colloids, with special reference to hrewing (KING) 2.

WILKENING, LUDWIG: *Die Herstellung von Spiritus aus Melasse und Guanol aus Melasseschlempe.* Hanover: Wilh. Riemschneider. 1919.

Diastase. K. KASHIWAGI. Japan 36,279, Apr. 28, 1920. Dry germinated wheat or barley is crushed, treated with H₂O to ext. enzymes and sol. matters, and sep'd. from H₂O by a press. After drying the residue is mixed with starch, etc., and set aside for 30-48 hrs. at suitable temp. and humidity with a small quantity of malt, from which pure and strong diastase is extd. and pptd.

17—PHARMACEUTICAL CHEMISTRY

W. O. EMERY

Determination of nearsphenamine in a complex mixture. ALBERT MOREL. *Bull. pharm. de l'Est*, May 1920; *Répert. pharm.* 33, 43-4(1921).—In a mixt. consisting of HgI, KI, NaHCO₃, arrhenal, vegetable matter, and 0.6% of nearsphenamine, the latter was detd. as follows: 3 g. of the mixt. were treated with dil. HCl (1:10) and the soln. was filtered. An equal vol. of a 10% soln. of dimethylaminobenzaldehyde in dil. HCl (Erlach and Berthelm's reagent) was then added. At the end of 24 hrs., the mixture was centrifuged and the orange-colored deposit, containing the nearsphenamine, washed to remove HCl and arrhenal. After digestion with H₂SO₄ to destroy organic matter, and subsequent oxidation, the As was detd. with the aid of the Marsh apparatus. The identity of the arsenic compound was further established by the fact that the distillate obtained by heating the mixture with H₂SO₄ gave a positive reaction for formaldehyde. A. G. DuMez

New digitalis experiments, judging and treatment of the drug in practice. R. WASICKY. Univ. Vienna. *Pharm. Monatshefte* 1, 169-75(1920).—An address dealing with both cultural and biological expts., demonstrating among other things that the glucosides occur in the mesophyll, that afternoon leaves have a higher glucoside content than those picked in the morning, that the leaves contain a glucoside-splitting enzyme. It further appears that 1st- and 2nd-year plants are equally effective, that both cultivated and wild plants are equally permissible, so far as *Digitalis purpurea* is concerned. The drug should be dried at 60° and standardized by means of a simple biological method, the details of which should be definitely fixed. W. O. E.

Evaluation of Peru balsam. H. WOLFF. *Pharm. Ztg.* 66, 38-9(1921).—A discussion of the tests as developed by Dieterich, Herzog, Fromme and others, whereby W. arrives at the conclusion that not only the color tests but also the petr.-ether test via Enz-Hager should be applied before a decision as to purity. W. O. E.

Behavior of albumins and antitoxins towards the electric current and isolation of pure antitoxic albumin from diphtheric serum by the electro-osmotic method. W. G. RAPPEL. *Ber. pharm. Ges.* 30, 314-28(1920).—It is shown experimentally that antitoxic albumin is obtainable in a pure state from diphtheric serum by treatment with the elec. current in a divided cell, the inner portion of which contains the serum and is sepd. from the outer portion containing the electrodes and H_2O by appropriate semi-permeable membranes. After the removal of electrolytic impurities, euglobulin is pptd., paraglobulin and albumin being thereupon sepd. from the filtered soln. by virtue of higher elec. charge and hence greater rate of migration. The antitoxin occurs for the most part in combination with the paraglobulin. W. O. E.

Spanish oil of thyme, and estimation of thymol. H. MASTBAUM. *Chem.-Ztg.* 45, 18-9(1921).—The Spanish oil has its source in 4 different species, having a phenol content varying from 40 to 60%. To evaluate in terms of thymol, shake 25 g. of the oil with 100-, 80- and 50-cc. portions of 5% NaOH soln., allowing the mixt. to stand $\frac{1}{2}$ hour before withdrawal of the caustic soln. Collect the aq.-alk. liquid in a 250-cc. flask, fill to mark, mix thoroughly and pass through a dry filter. Acidify a 200-cc. aliquot (= 20 g. substance) in a short-stemmed separatory funnel with concd. HCl, allow the pptd. phenol to agglomerate and the liquid to cool, withdraw the acid soln.; run the phenols into a tared beaker containing a glass rod, and weigh. On stirring or seeding with a trace of thymol, the latter substance soon separates as tablets, especially if cooled in ice H_2O . As soon as there is no further apparent increase in crystals, transfer to a weighed filter and draw off the oil by suction. Remove adhering oil by pressing between filter paper. The % of thymol is ascertained by a series of calculations involving the wts. of beaker, glass rod, filter, and amount of phenols clinging thereto after the final weighing of loose crystals. An illustration of such calcn. is given. W. O. E.

Labelling of concentrated hydrogen peroxide solutions. ANON. *Chem.-Ztg.* 45, 124 (1921). A discussion of certain misunderstandings arising from labelling H_2O_2 solns. with respect to both wt. and vol. percentages. W. O. E.

Isolation of the active sulfur components of crude ichthyol, and related shale oils. H. SCHEIBLER. *Pharm. Monatshefte* 1, 148(1920); cf. *C. A.* 14, 1982.—An address (cf. following abstract). W. O. E.

Purification of shale oils (ichthyols) rich in sulfur for medicinal purposes. H. SCHEIBLER. *Pharm. Monatshefte* 1, 182(1920).—The process consists essentially in treatment of the crude oil at 170° with soda-lime, then, after distn., treatment of the distillate with Na or $NaNH_2$, whereby evil-smelling and colored constituents are eliminated. The resulting bright yellow oil, of faint not unpleasant odor contg. C, H and S, b. 100 to 300° . From certain fractions homologs of thiophene were isolated, which appear to constitute the active S principles of ichthyols. W. O. E.

New reaction for detecting quassia. C. GLUECKSMANN. *Pharm. Monatshefte* 1, 176-80(1920).—The following summary is given: (1) Instead of prepg. the ext. with H_2O , a mixt. of equal parts of alc. and H_2O is recommended. (2) The dry ext. thus prepd. shows the following characteristics: (A) A trace dissolved in H_2O , and the resulting soln. dild. until colorless, must possess a distinctly bitter taste. (B) About 5 cc. of an alc. soln. of the ext. prepd. in the proportion of 1 part ext. to 50 parts of strong alc. acquires after the addition of a trace of phloroglucinol with about 5 cc. fuming HCl a rose-red color. (3) The detection of Tinct. quassiae may be effected by adding to 5 cc. of sample a trace of phloroglucinol and 5 cc. fuming HCl. After mixing a rose-red coloration soon develops. W. O. E.

Aluminium formate. R. WOLFFENSTEIN. *Pharm. Ztg.* 65, 1018-9(1920).—*Polemical in re "Ormicet"* (cf. *C. A.* 14, 2678). W. O. E.

Ornicet. F. RABE. *Pharm. Ztg.* 66, 72(1921).—A reply to Wolfenstein's paper on Al formate (cf. preceding abstr.). R. WOLFFENSTEIN. *Ibid.* 72.—Polemical. W. O. E.

Savior sodium. G. KAWASHIMA. *Tokyo Iji Shinji* No. 2070, 759-62(1918); *Jap. Med. Literature* 5, 43(1920).—Savior sodium is described as "a dioxy-diamino-Na compd. of arsenobenzene" alk. in reaction, readily sol. in water, and containing approx. 20% As. Savior (a related compd. containing 30% As) was injected subcutaneously into 8-day mice in a dose of 2.5 mg. per 10 g. of body wt.; one-half the exptl. animals were killed. JOSEPH S. HEPBURN

The cinchonas. EM. PERROT. *Rev. prod. chim.* 24, 45-7(1921).—A brief review of the history of the use of cinchona bark, of the natural habitat of the tree and of the places where it has been successfully acclimatized, of the method of collecting the bark in the forest, of the history of the cultivation of cinchonas, and of the present state of the cinchona and quinine markets. A. P.-C.

Future of the essential-oil industry in Japan. RINOSUKE SHINOZAKI. *J. Chem. Ind. (Japan)* 23, 747-63(1920).—Manuf. of camphor and peppermint oils represents 2 great essential-oil industries in Japan; much less important industries are the manuf. of turpentine, *Kumosi*, orange, lemongrass, citronella, and cedar oils. Amts. of yearly production, method of purification and identification, and physical and chem. characteristics of these oils are given. Future development of camphor oil depends on cultivation of the plant, and further investigation on the best method of extn. from the leaves and stems. Scarcity of land in Japan may interfere with its development; cultivation in Southern China is a possibility. In the peppermint-oil industry, more research will be necessary for proper examn. of grades of oil as well as for better methods of sepn. The turpentine-oil industry should be greatly improved, e. g., by increasing speed of extn. The future of the essential oil industry depends in no small degree on the promotion of perfume manuf. S. T.

Estimation of santonin in wormseeds. TATSUO KARIYONE AND YUSHIRO KIMURA. *J. Pharm. Soc. Japan* No. 403, 927-40(1920).—The method is based on the lactone character of santonin. This method first used on cryst. santonin by Katz is applied by the authors to wormseeds with several modifications. 10 g. of pulverized wormseeds are extd. with ether for 3 hrs. in a soxhlet. After removal of ether, 100 cc. of 5% Ba(OH)₂ is added to the residue and the mixt. boiled under a reflux condenser. When cooled, dry CO₂ is passed through the soln. until it becomes acid to litmus; it is filtered quickly under suction. 80 cc. of the filtrate is shaken vigorously in a separatory funnel, for 2 minutes after additions of 10 cc. of 15% HCl and 20 cc. CHCl₃. After standing a few minutes, the CHCl₃ layer is filtered into a glass bottle through a filter paper moistened with CHCl₃. After the 3rd extn. with 10 cc. of CHCl₃ the filter paper is washed with a little CHCl₃. The CHCl₃ is carefully evapd. off and 30 cc. of alc. is added to the residue, which is dissolved by boiling. The soln. is neutralized with 0.1 N KOH (with phenolphthalein as indicator), 20 cc. more of 0.1 N KOH is added and boiled for 30 min. under a reflux condenser. With addition of 0.5 cc. of the same indicator, the soln. is titrated with 0.1 N HCl until excess of 1 drop will turn the red color to yellow. As a control 20 cc. of 0.1 N KOH is boiled under the same condition. The % of santonin (*P*) in wormseeds is $P = [(S' - S) \times 2.462]/8$ where *S'* = cc. of 0.1 N HCl used for the control and *S* = cc. of the acid used for the unknown. The error of detn. made with known amt. of santonin was less than 0.029%. Data are given to show that the Katz method gives too low figures, while this new procedure brings the result much nearer to the theoretical values. S. T.

Constituents of the Korean ginseng. III. HEISABURO KONDO AND UMETARO AMANO. *J. Pharm. Soc. Japan* No. 466, 1027-43(1920); cf. C. A. 9, 2793; 13, 361.—

The chem. compn. of the saponin found in the MeOH ext., and comparison of the chem. constituents of Korean and Japanese ginseng are reported here. Since Pb seems to adsorb certain amts. of the saponin, the original method of extn. is modified as follows: The Pb acetate ppt. is dried, and extd. with MeOH in a soxhlet, the alc. is evapd., the residue dissolved in H₂O, Pb is removed by H₂S, and the sugar and other compds. are pptd. by dil. H₂SO₄ and filtered off. The filtrate is neutralized with NaOH, evapd. and recrystd. from MeOH and Et₂O. The amts. of saponin thus prepd. were 0.3% from Japanese (*Aidu*), 0.3% Korean (root hairs), and 0.15% Korean (roots) ginsengs. It b' about 220° and $[\alpha]_D^{16} = -24.09$. On hydrolysis with a large amt. of 7% alc. HCl for 15-6 hrs. there were obtained 2 new compds. *panax-sapogenol* and *panax-sapogenol*, *amorphous*. (1) The yield of panax-sapogenol was 1.5% of the original sample and 45% of the saponin. It m. 242.5°, $[\alpha]_D^{19} = 20.12^\circ$ (in alc.), white long columnar crystals, insol. in H₂O, Et₂O, sol. in alc. and glacial AcOH, negative test with FeCl₃, gives cholesterol reaction. Analysis shows the formula (C₄₇H₈₀O); it has 3 OH groups. Its Ac deriv. m. 203°, is sol. in Et₂O, alc., glacial AcOH, but not in H₂O. Bromination shows it has one ethylene group. Hydrogenation gives white needles, m. 246°, sol. in H₂O alc. and glacial AcOH, but insol. in Et₂O. $[\alpha]_D^{20} = 13.29$ (in alc.). The amorphous fraction, named *panax-sapogenol*, *amorphous*, C₄₇H₈₀O, is shown in every respect to be an isomer of the cryst. panax-sapogenol. It m. 130°, gives the cholesterol reaction, is sol. in alc., Et₂O and glacial AcOH, but insol. in H₂O and petroleum ether, $[\alpha]_D^{18} = 23.40^\circ$. Its Ac deriv. m. 120°. Its hydrogenation product m. 132°, has $[\alpha]_D^{18} = 19^\circ$. The last hydrolytic products are glucose and pentose. From these analyses the authors conclude that the mol. wt. of the original saponin is 876, and that it consists of one mol. of panax-sapogenol, 2 of glucose, and 1 of pentose. Both Korean and *Aidu* ginsengs give identical saponins, as well as essential and fatty oils. S. T.

Perilla oil and *Chamaecyparis* (Japanese cedar) oil. YŪSHICHI NISHIZAWA. *J. Tokyo Chem. Soc.* 41, 1039-42(1920).—The compn. of aldehyde-free perilla oil is first given. After the aldehyde is removed and ether evapd. by passing CO₂, the oil is dehydrated with anhydrous Na₂SO₄. It has $d_{44} 0.9169$, $n_{44} 1.49632$, and $[\alpha] 108.7$. When the original oil is distd. at low pressure, about 50% distills at 110-15°, and 115-20°; when purified this b₁₆ 112-13°; and contains C 80.6%, H 9.52%, mol. wt. 148; its oxime, m. 100-1°, corresponds to that of Semmler and Zaar's perillaldehyde (cf. *C. A.* 4, 2810). The fraction of the oil b₁₆ 60-80° after shaking with Na₂SO₄, is free from aldehydes. When purified it b₁₆ 45-50°, h. 180°, d. 0.850, $n 1.470$, $[\alpha] -89$, mol. wt. 130, C 87.1%, H 11.6%; its bromide m. 103-4, showing it to be limonene. Pinene is identified in Japanese cedar oil. The fraction (70-80%) b₁₆ 60-1°, h. 156-7°, d. 0.850, $n 1.467$, $[\alpha] 45.20$, C 87.81%, and H 11.87%. Its nitroschloride m. 101°, corresponding to the nitroschlorides prepd. from pure pinene, and its HCl salt m. 125°. S. T.

Determination of aminohydroxyphenyl arsenious oxide in arspenamine. H. COUSIN. *J. pharm. chim.* 22, 390-2(1920).—P. Ehrlich (*C. A.* 6, 1616) has pointed out the formation of the 20 times as toxic AsO.C₆H₄-3-NH₂-4-OH (A) from arspenamine (S) by the O of the air, also a simple method of its detn. Dissolve 1 g. of S in 10 cc. MeOH; add about 80 cc. H₂O; a limpid, golden yellow soln. should result. Then add 1.5 g. of pure pptd. CaCO₃ and shake; the base of S is pptd., A is in soln. Complete to 100 cc., filter, and to 50 cc. of the colorless filtrate add 75 cc. H₂O, 5 cc. N HCl, a little starch paste and titrate with 0.05 N I soln.; 1 cc. thereof indicates 1% of A. S of good quality should contain not more than 0.5-0.8% of A. Two samples having caused accidents, contained 2.3 and 2.43%; a pre-war sample examd. early in 1919, 2.6%; another, visibly altered, 3.2%; 8 others varied from 1.9 to 1.09%. S. WALDBOTT

Industrial and agricultural chemistry in the British West Indies (BROWN) 13. Distillation [in winning of essential oils] (DURRANS) 13. Camphor synthesis (WITTE) 10.

A water-insoluble compound containing guaiacol and calcium. T. KÔNO and K. ISHINO. Japan 36,268, April 28, 1920. A basic Ca guaiacolsulfonate, $[\text{C}_6\text{H}_4(\text{OCH}_3)_2(\text{OH})(\text{SO}_3\text{Ca})]_2\text{O}$, is prepd. by mixing 80 g. Ca guaiacolsulfonate soln. with 300 g. lime water, filtering and drying *in vacuo* at 120° to const. wt. The product is not hygroscopic; it is sol. in the stomach.

A water-insoluble compound containing guaiacol and alkaline earth metals. T. KÔNO and K. ISHINO. Japan 36,269, April 28, 1920. Alkali guaiacolsulfonates give water-insol. salts by reaction with alk. earth salts. Basic Ca guaiacolsulfonate (preceding abstract), *e. g.*, is prepd. by dissolving 100 g. K guaiacolsulfonate in 300 g. H_2O , mixing with a satd. soln. of CaCl_2 , to which 300 g. NH_4OH are added, filtering, washing with H_2O and drying *in vacuo* at 120° .

18—ACIDS, ALKALIES, SALTS AND SUNDRIES

The manufacture of nitric acid. F. C. ZEISBERG. *Chem. Met. Eng.* 24, 443-5 (1921).—A description of the vertical or pot retort manuf. of HNO_3 includes the retorts, condensers, absorption system, storage and transportation, and yields now reach 99% Peace-time and war-time uses of HNO_3 are enumerated. W. H. BOYNTON

Concentration of nitric acid from the manufacture of nitrated explosives. H. LÉMAITRE. *Rev. chim. ind.* 29, 380-5 (1920).—Brief and general discussion of the concn. of HNO_3 by heating with concd. H_2SO_4 . A. P.-C.

Phosphoric acid evaporation. H. E. LABOUR. *Chem. Met. Eng.* 24, 466-8 (1921).—The principal difficulties encountered in the use of vacuum evaporators for concg. H_3PO_4 are corrosive action due to F and heavy scale formation consisting principally of CaSO_4 . Towers, both packed and open, were tried but the deposition of scale and formation of metaphosphate caused serious loss. In order to reduce the corrosive action and to eliminate metaphosphates, a new method was devised which carried out the evapn. without raising the temp. of the liquid to the b. p. A spray machine atomizing the liquid by throwing it from the surface of a revolving disk was adopted and the acid was evapd. by contact with heated air. Scaling trouble is not encountered; thus there is uniform economy of operation. S. D. KIRKPATRICK

Present and future of the sulfuric acid industry in Japan. SÔSUKU NAKAGAWA. *J. Chem. Ind. (Japan)* 23, 676-81 (1920).— H_2SO_4 was first imported to Japan by the English in 1871. At present there are 111 manufg. houses, 4 of which manuf. acid from ZnS , 8 from S, and 99 from the iron sulfide. In 1919, over $1\frac{1}{2}$ million tons were manufd., the total capacity of all these plants being nearly one million tons. The future of this industry depends on the discovery of catalyzers other than Pt, solution of the supply of raw materials, and enlargement of the scale of manuf. S. T.

Glover and Gay Lussac tower lining and filling. ANON. *Australasian Chem. Met.* 3, 51-7 (1920).—A practical discussion. JEROME ALEXANDER

Ammonia oxidation units for sulfuric acid plants. WILFRID WYLD. *Chem. Age (London)* 4, 150-1 (1921).—This paper discusses the possibility of using the NH_3 converter in place of NaNO_3 for providing the necessary N oxides in the manuf. of H_2SO_4 . Directions are given, and reference is made to the precautions to be observed for the most efficient operation of the new process. W. H. ROSS

The present status of the synthesis of ammonia at high pressures. GEORGES CLAUDE. *Compt. rend.* 172, 442-4 (1921); cf. C. A. 15, 576.—A review of the latest progress made in the synthesis of NH_3 by the Claude process. C. B. DURGIN

Manufacture of synthetic ammonia at Oppau, Germany. III. ANON. Chem. Met. Eng. 24, 391-4(1921); cf. C. A. 15, 1191.—The process of making $(\text{NH}_4)_2\text{SO}_4$ by passing CO_2 gas into a suspension of powdered gypsum in NH_4OH is outlined. The plant can treat 1000 tons of gypsum daily. The reaction lasts from 9 to 10 hrs. The process is carried out in cone-bottom tanks equipped with stirrers. The CO_2 is introduced at several points. The NH_3 enters at one. Towers aid in the recovery of NH_3 . The gypsum and water are in "paste" consistency. The mixt. is treated in a series of tanks in which it is presumably meeting purer CO_2 as the reaction nears completion. Agitation continues. The CaCO_3 is filtered on leaves like those used in slime filtration in the "Cyanide" process for Au extn. The cake is afterward blown off and washed away. $(\text{NH}_4)_2\text{SO}_4$ soln. of 25% strength is produced. This is evapd., crystd., centrifuged and the product stored. The manuf. of Na_2CO_3 and NH_4Cl from salt, NH_3 and CO_2 is carried out by the Solvay process. 78 parts of NH_3 are required for 279 of salt. The NH_3 acts for about 2 hrs. and the CO_2 for 18 hrs. NH_4NO_3 is made from HNO_3 and NH_3 . The soln. is evapd. under vacuum and the product crystd. It is mixed with KCl and sold as a fertilizer or it is sold direct. The manuf. of catalysts is mentioned but is not described. In the *coke plant*, about 850 tons of coal produced daily 650 tons of coke and the usual amts. of gas, NH_3 and other by-products. In the *power plant*, 2400 tons of lignite briquets, equiv. to 1300 tons of coal, are burned daily. There are 356 sq. m. of grate surface and one ton of steam is made hourly per sq. m. of grate. The *water supply plant* and the *coal handling plant* are described briefly. In the lab., 20 chemists and 60 subordinates are working on research problems. Diagrams of the plant lay-out and of the principal parts are shown. The cost of the plant was about \$75,000,000. On the basis of pre-war prices, it was making NH_3 at about 8 c. per lb. Abundance of fuel and good river transportation made this possible. The French are planning to make NH_4Cl instead of $(\text{NH}_4)_2\text{SO}_4$. Waste CaCl_2 from the Solvay soda process is to be used.

JAS. O. HANDY

The nitrogen question. PAUL PASCAL. Rev. sci. 58, 740-6(1920).—After discussing the vital importance of fixed N for fertilizers and explosives, P gives figures prepd. by Toniolo showing the advantage of the Haber process (as compared with the flaming arc and cyanamide processes) in installation, power, and production costs. The enormous growth of German fixed N production is tabulated against that of other countries, and a note of warning sounded against the danger of a German hegemony in fixed N.

JEROME ALEXANDER

The commercial fixation of nitrogen as cyanides. TH. THORSSELL. Z. angew. Chem. 33, 1, 239-40, 245-7, 251-4(1920).—A chronological review of the processes of fixing N in the form of cyanides together with a discussion of the reactions involved.

C. B. DURGIN

The American potash industry and its problems. JOHN E. TREELE. J. Ind. Eng. Chem. 13, 249-52(1921).—A review of the American potash industry with special reference to the problems that were encountered in the com. recovery of K_2O from the brine of Searles Lake, Calif.

W. H. ROSS

Natural barium sulfate. CH. COFFIGNIER. Rev. chim. ind. 29, 368-6(1920).—A general description of the purification of natural BaSO_4 , with a comparison of the properties of French, Spanish, and Italian BaSO_4 .

A. P.-C.

British barytes production. JOHN RAMSDEN. Chem. Trade J. 68, 203-4(1921).—A report of a conference of British barytes producers in which the quality of the German and English products, the cost of production and the necessary improvement in the industry are considered. In the grading instrument of Lowy a current of H_2O travelling at the rate of 7 mm. per sec. carries the finer particles with it while the coarser particles are left behind in a graduated tube. The grade of the product is indicated

by the amt. of residue in the tube. Treatment of the natural product with dil. H_2SO_4 removes all the color except the pink.

G. W. STRATTON

Preparation of ferric sulfate from pyrites ash and filter cake. A. HUTIN. *Rev. chim. ind.* 29, 349-50 (1920).—The following process is proposed for the prepn. of $\text{Fe}_2(\text{SO}_4)_3$ for the coagulation of blood in abattoirs, the deodorization of putrid meats and fish, etc. 40 kg. of Fe_2O_3 (in the form of pyrites ash) are added in small portions, with vigorous agitation, to 180 kg. of NaHSO_4 (containing 40.8% free H_2SO_4), which has been slightly heated. The reaction is very violent, necessitating the use of very large receptacles. Heating is continued until all the H_2O formed has been driven off, as the final product must be quite dry. The process has been tried out at the works of Jodet Angibaud at La Rochelle, but would require to be further tested out. A. P.-C.

The outlook for the magnesite industry. ANON. *J. Elec. West Ind.* 46, 245-6 (1921), 2 illus.—Extensive deposits of cryst. magnesite occur in Stevens Co., about 60 miles from Spokane, Wash. American interests control approx. 80% of the magnesite deposits of the world. The daily consumption of plastic magnesite in the U. S. is about 100 tons; it is used in a cement which has enduring qualities and sets speedily.

C. G. F.

Progress of chemicals. SHUICHRŌ OCHI. *J. Chem. Ind. (Japan)* 23, 733-47 (1920).—Only *Cl* and *acetylene* are considered. Proper disposition of *Cl* formed as a by-product from soda manuf. is suggested. In Japan, approx. 75 million lbs. of soda are consumed, manuf. of which will yield 165 million lbs. of bleaching powder as a by-product. The annual use of the powder in Japan is only 33 million lbs. If the competition for the soda market is to be maintained, study must be made of the utilization of the *Cl* thus formed. Manuf. of liquid *Cl*, *HCl*, chlorination of hydrocarbons, utilization for certain metallic and organic chlorides are discussed. 100 million lbs. of carbide are produced, of which 35 million lbs. are used for acetylene manuf. How to dispose of the acetylene is considered. Recent progress in the manuf. of C_6H_6 , aldehyde, alc. and AcOH from acetylene is reviewed, showing the cost of manuf. of all these compds. on the basis of the present price of carbide, which is about 2 cents per lb. S. T.

The arsenic industry. GEORGES VIF. *Industrie chimique* 7, 426-9 (1920).—A description of the process of manuf. of crude and refined As_2O_3 . Also in *Chem. Met. Eng.* 24, 527-8 (1921).

A. P.-C.

Sanitary measures to be taken in the chlorine industry. PAUL RAZOUS. *Industrie chimique* 8, 13-4 (1921).—General outline of the dangers to the health of the workmen in the *Cl* industry, and of the measures by means of which they can be reduced to a minimum or eliminated.

A. P.-C.

Possible developments in hydrogen manufacture. F. K. RIDGAL. *J. Soc. Chem. Ind.* 40, 10-4T (1921).—R. discusses the theories and operation of *H* from the steam-*Fe* processes, the water-gas catalytic process, and the process of direct production of *H* from coke. The Linde-Frank-Caro method delivers *H* free from all impurities except CO (2-4%) and conveniently under pressure, but the CO content and cost of operation are disadvantages. An inversion method was developed during the World War, whereby finely divided Fe_2O_3 was blown through a pipe by means of hot water-gas and the reduced oxide transferred to another pipe, also maintained at suitable temps. for oxidation with steam. This method offers commercial possibilities in economical utilization of spathose—in size of plant required and the almost certain increase in the activity of the material in this form. For direct production from coke the methods based on reactions of the water-gas producer are promising: (I) $\text{C} + \text{H}_2\text{O} = \text{CO} + \text{H}_2$; (II) $\text{CO} + \text{H}_2\text{O} = \text{CO}_2 + \text{H}_2$; (III) $\text{C} + \text{CO}_2 = 2 \text{CO}$. It is necessary to operate at a low temp. and the reactions (I) and (II) may be accelerated by simultaneous employment of pressure and a catalyst. The reaction is heterogeneous and catalytic stimulation is consequently

difficult. For water-gas generators operating at high temps. (1800°) any increase in constituents forming clinker or fusible slag is to be avoided, but at 600-700° a small increase is permissible. Inversion of the process appears possible whereby powdered coke would be sprayed with a catalytic material and then injected into a current of superheated steam. This obtains simultaneous increase in reaction velocity and elimination of the clinker problem.

W. H. BOYNTON

Compressed-gas industry in Japan. YOSHIKIYO OSHIMA. *J. Chem. Ind. (Japan)* 23, 670-5(1920).—Manuf. of compressed O in 1911 was the first industry of this kind in Japan. At present, 15 houses make it from the air, and 10 houses from the decompn. of H_2O . About 30,000 cu. m. of H is annually produced in Japan. Only one concern makes NH_3 , producing about 100,000 lbs. yearly. 800,000 lbs. of CO_2 , 50,000 cu. m. of acetylene annually and 800 lbs. of Cl daily are the present capacity of these most promising compressed-gas industry. Most of the containers for these gases are imported. The manuf. of these containers, proper regulation for the transportation and better methods of manuf. of these gases are urged.

S. T.

Composition of bird-lime. YUSHICHI NISHIZAWA. *J. Tokyo Chem. Soc.* 41, 1043-8(1920).—Practically $\frac{1}{2}$ of bird-lime can be extd. with ether. All of the active principle of the lime is in this ether ext., which when freed from ether, is an elastic, gum-like, semi-transparent, yellowish green substance. Aq. KOH will not saponify com. bird lime, but when alc. KOH (80 g. per l.) is used in a ratio of 5-600 g. of the substance with 3.5 l. of alc. KOH, the sapon. is complete in 10 days (over the steam bath). From the soap were sepd. palmitic and elaidic acids, identified by their m. ps. and by their lead salts.

S. T.

The hyposulfites (DUBOSC) 6. Vegetable decolorizing carbons (BRADLEY) 28. Nitrogen and nutrition (LASSWITZ) 15. Cottrell system of dust and fume precipitation [in sulfuric acid manufacture] (ANON.) 4. Helium (MOORE) 2. Phosphate in Canada (SPENCE) 8. Equilibrium of the four-component system: sodium sulfate, sodium bicarbonate, ammonium sulfate, ammonium bicarbonate (NISHIZAWA) 2. Decomposition pressure of the saturated aqueous solution of ammonium bicarbonate (NISHIZAWA) 2.

Ammonium phosphate. H. C. HETHERINGTON and J. M. BRAHAM. U. S. 1,369,763, Feb. 22. A soln. of crude H_3PO_4 of an initial strength of about 68-72% or higher is constantly fed into a saturator through the acid and NH_3 is fed in adjacent to the bottom so that the soln. in the saturator is preferably maintained slightly acid. Crystals formed are continuously removed from the soln. while the latter is slightly acid and mono- NH_4 salt without contamination with di- NH_4 salt is thus obtained. Owing to the heat generated by the process a sep. evapn. step is dispensed with and evapn. and crystn. are obtained in the vessel without external heating. When 60% H_3PO_4 is used a temp. of about 108° and with 85% H_3PO_4 temps. up to 120° or slightly higher are attained. The use of 68-72% acid is preferable because at the temps. attained when acid of this strength is used there is no appreciable formation of di- NH_4 salt or over-concn. with its attendant danger of the crystals occluding viscous acid. The crystals of the $NH_4H_2PO_4$ removed from the saturator are drained and centrifuged and may be further dried if it is desired to remove the last traces of mother liquor.

Anhydrous zinc chloride. P. DANCKWARDT. U. S. 1,360,729, Feb. 22. Oil sludge from the treatment of petroleum oil with $AlCl_3$ is heated with Zn ore in such proportions that at the temp. employed all the Cl of the $AlCl_3$ will combine with the Zn. The $ZnCl_2$ thus formed is volatilized and condensed. Al_2O_3 remains in the residue and is recovered as a by-product after burning out the C from the residue. The oil residue

and Zn ore may be ignited and supplied with air and steam to promote the reaction and remove the C as a fixed gas. Zn oxide, carbonate or roasted sulfide ore may be employed.

Compound of urea with calcium nitrate. C. BOSCH. U. S. 1,369,383, Feb. 22. A compd. corresponding to the formula $\text{Ca}(\text{NO}_3)_2 \cdot 4\text{CO}(\text{NH}_2)_2$ is obtained by mixing the constituents in the required proportions in the presence of a small quantity of H_2O and then drying or by adding to a bot. concd. soln. of $\text{Ca}(\text{NO}_3)_2$ or to a melt of a hydrate of this salt a suitable proportion of urea and allowing crystn. to ensue. Long exposure of the salt or its solns. to a high temp. should be avoided as even temps. below the b. p. may cause decompn. with pptn. of CaCO_3 . The double compd. is easily sol. in H_2O and does not liquefy if exposed to the air. It is especially suitable for use as a fertilizer.

Phenol-formaldehyde condensation product. A. W. WYLLER and W. T. ROBINSON-BINDLEY. U. S. 1,368,887, Feb. 15. See C. A. 15, 1060.

Phenol-formaldehyde condensation products. F. POLLAK. U. S. 1,369,352, Feb. 22. Light-colored products resistant to the action of air and light are obtained under the following precautions: (a) The amt. of catalytic or condensing agents of acid or basic character used in the initial reaction between the phenol and active-methylene-containing substance should be kept as low as possible; (b) the phenol still present in the reaction product should be removed by repeatedly shaking the mass with H_2O at a temp. below 40° ; (c) the soap-like mass obtained by this treatment should be washed with neutral solns. and H_2O . Cryst. PhOH 100 and 40% CH_2O soln. 80 parts may be heated under a reflux condenser with 0.2 parts PhONa until the condensation product is pptd. The heavier resinous layer is sepd. from the supernatant aq. layer and is shaken repeatedly with 100 parts H_2O . The soap-like product is well washed with H_2O containing 10% MeOH and afterward is washed with cold H_2O and the residue is freed from the last traces of PhOH by distn. *in vacuo* and is then molded and by heating to $95\text{--}120^\circ$ is converted into an infusible and insol. product. By using an equal amt. of a 3% H_2O_2 soln. instead of MeOH , a somewhat darker but light- and air-proof product is obtained. α -Polyoxymethylene, PhOH and very dil. H_2SO_4 may be used as the initial reaction mixt. and the product washed with H_2O and dil. H_2O_2 soln. An intermediate product thus formed can be combined with additional CH_2O to obtain a light- and air-proof material. The addition of mild catalysts at the end of the washing (to facilitate final hardening) does not affect the resistance of the product to light and air.

Electric insulator. M. KUBO and the SHIBaura MFG. Co. Japan 36,073, Apr. 5, 1920. Vegetable drying or half-drying oil, concd. by heating at $150\text{--}320^\circ$, is painted on a thin paper, on which thin slices of mica are spread and then painted with the oil and mica alternately to suitable thickness and dried at 100° for 10–30 hrs.

19—GLASS, CLAY PRODUCTS, REFRACTORIES AND ENAMELED WARE

G. E. BARTON, C. H. KERR

Recent progress of the ceramic industry. KIYOHARU KONO. *J. Chem. Ind. (Japan)* 23, 764–75 (1920).—Progress of this industry in Japan is represented by incorporation of 107 new manufg. houses in 1919. Past and present activities are discussed for manuf. of bricks, pipes, tiles, fire-proof utensils, china ware and other porcelain, glass, for plate and bottle, silicate glass, elec. globes, and cements. S. T.

British scientific glass industry. EDWARD QUINN. *J. Soc. Chem. Ind.* 40, 6–7r (1921).—A brief history of the development of the lab. and optical glass industry in the British Empire during the war, directed as an argument for protection against foreign competition. D. E. S.

Scientific glassware made at Vineland, N. J. *Glassworker* 40, No. 19, 19(1921).—A general description is given of the methods of making chem. ware, lab. app. and thermos bottles. Most of these products replace those imported from Germany and Austria before the war.

R. J. MONTGOMERY

Hints on the melting of watch glasses. *Schnurpfel's Review for Glass Works* 4, No. 47, 767(1921).—Three qualities are made, finest, medium and ordinary. Satisfactory batches are given. 1st grade: Sand 100, potash 35, lead 35, saltpeter 5, lime 10, MnO_2 $1/4$. 2nd grade: Sand 100, potash 35, barytes 10, lime 10, saltpeter 3, As $1/2$, MnO_2 $1/4$. 3rd grade: Sand 100, potash 17, soda ash 17, saltpeter 2, lime 14, As $1/2$, MnO_2 $1/4$. The glass must be absolutely free from bubbles, blown into large balls of correct curvature and uniform thickness. After annealing the watch-glass panes are cut out and finished.

R. J. MONTGOMERY

Composition of selenium ruby glass. *Schnurpfel's Review for Glass Works* 4, No. 47, 771(1921).—Sand 100, soda ash 42, borax 12, lime 8, Se 1.25, CdS 1.75. The glass is used for lantern globes.

R. J. MONTGOMERY

Composition of glass for lamp chimneys. *Schnurpfel's Review for Glass Works* 4, No. 47, 771(1921).—Sand 100, soda ash 33, lime 10, PbO 6, barytes 6, borax 1, saltpeter 2, Mn 0.25.

R. J. MONTGOMERY

A glass-etching ink. *Schnurpfel's Review for Glass Works* 4, No. 47, 771(1921).—Take 2 parts of HF, 2 parts of NH_4F and 2 parts of pptd. BaSO_4 and rub together in a china mortar. Transfer to a Pb cup, add fuming HF and stir with a gutta-percha rod.

R. J. MONTGOMERY

Double refraction and crystalline structure of silica glass. LORD RAYLEIGH. *Proc. Roy. Soc.* 98A, 284-96(1920); cf. *C. A.* 14, 327, 604.—Silica glass when examined with a special polariscope shows double refraction, which is due not to stress but to a cryst. structure. This double refraction is of the order of magnitude of one-sixtieth that of cryst. quartz, and usually appears as a structure of doubly refracting grains about one-half mm. in size with no regular orientation. If the grained material is drawn out while hot, the grains elongate into fibers following the course of the material, and show "straight extinction" in the polariscope, their length being along one axis of the ellipsoid of optical elasticity. Optical silica disks show a spiral structure. By heating and cooling such a disk the structure may be made to disappear and reappear.

DONALD E. SHARP

The devitrification of glass. HARRISON W. CRAVER. *Diamant* 42, 379; *Glass Ind.* 1, 40(1920).—A brief description of the process of devitrification.

DONALD E. SHARP

Use of light soda ash in the production of flint bottle glass. C. A. COLE. *Glass Ind.* 1, 34-8(1920).—Lime batch containing light soda ash may be melted in glass tanks without a tendency toward formation of scum or seeds if high temp. and uniform methods of feeding are employed. A melting temp. of 2450°F . (1340°C .) is recommended. Analysis of batch and resultant glass show that little alkali is lost in melting.

DONALD E. SHARP

The occurrence of crust or scum on continuous bottle tank furnaces. WILBUR F. BROWN. *Glass Ind.* 1, 29-30(1920).—Crust or scum in the melting chamber of glass tanks is usually high in SiO_2 and Na_2O but low in CaO . The causes of its formation are, a "cool" tank, or a batch of too high SiO_2 or CaO content. It can best be removed by using a proper batch and maintaining high temps., not by adding the common fluxing materials. Analysis of two typical scums are given.

D. E. SHARP

Permeability of glass to iodine and bromine vapors. JAMES BRERLY FERTH. *J. Chem. Soc.* 117, 1802-3(1920); cf. *C. A.* 8, 1894.—A continuation of an attempt by

F. to repeat Zengheli's expts. (C. A. 3, 973; 4, 1919). Glass is impermeable to I and Br under ordinary conditions. However, after 9.5 yrs. I had diffused slightly through the walls of glass tubes 0.208 mm. thick in one case, and 0.211 mm. thick in another case. In the first case there was a vacuum inside and outside the tube, and in the second case a vacuum outside and atm. pressure inside. The tubes were heated at 360° for 50 days during the first, and also the third year of the expt. Under the same conditions no Br passed through glass of the same thickness in 9.5 yrs. DONALD E. SHARP.

Clays and clay products. A. B. SEARLE. Third rept. on colloid chemistry, *Brit. Assoc.* (1920).—A very extensive (40 pp.) and suggestive discussion from the colloid-chemical point of view. JEROME ALEXANDER.

Report of the céramic division. JOSEPH KEELE. *Summary Report Can. Dept. Mines* No. 542, 102-9 (1920).—The occurrences and properties of fire, pottery and brick clays in eastern Ontario are described. Structural materials in Dundas, Stormont, and Glengarry counties, Eastern Ontario. J. KEELE AND L. H. COLE. *Ibid* 114-27. —Results of physical and firing tests of 15 clays and granulometric analyses of 13 sands are tabulated. Pottery clays. MARY F. YOUNG. *Ibid* 127-34.—Pottery clays and methods of testing and handling are described. Methods of making glazes, enamels and color decorations are given, also the occurrences of pottery clays in the Canadian provinces. L. W. RIGGS.

Possible uses for spent shale from shale-oil operations (THOMAS) 22. Analysis of chrome ores and chrome brick (ANON.) 7. The outlook for the magnesite industry (ANON.) 18. Applications of selenium (SUGIE) 2.

Coating glass to prevent accumulation of drops of water. J. H. T. ROBERTS. U. S. 1,369,708, Feb. 22. Accumulation of drops of moisture on glass is prevented by coating the glass with a thin layer of gelatin, agar, casein or similar transparent material.

20—CEMENT AND OTHER BUILDING MATERIALS

C. N. WILEY

Technical analysis of portland cement. W. O. ANDREWS. *J. S. African Assoc. Anal. Chem.* 3, 3-5 (1920).—Details are given of the usual methods for the detn. of SO_2 and insol. matter, SiO_2 , Fe_2O_3 , Al_2O_3 , CaO and MgO . G. W. STRATTON.

Central research laboratory for the cement industry. J. BIED. *Rev. ing.* 28, 1-7, 61-7 (1921).—Brief review of the present state of our knowledge of hydraulic cements and hints on the progress which might result in the cement industry from properly conducted research, to show the importance and advisability of establishing a central research lab. to be supported by the French cement industry. A. P.-C.

Will sodium fluoride come into general use for preserving wood? GEO. M. HUNT. *Chem. Met. Eng.* 23, 1123-4 (1920).—Although the desirability of NaF as a wood preservative is practically established, it cannot at present compete with ZnCl_2 in cost. Search for cheap sources of NaF is suggested; the waste gases from superphosphate manuf. offer a possible source of cheap F. JEROME ALEXANDER.

Possible uses for spent shale from shale-oil operations (THOMAS) 22. Cement and lime paper bags (HOUSTON) 23. Analysis of limestone, lime and hydrated lime (ANON.) 7. Investigation of dust in the air of granite-working plants (KATZ) 14. Structural materials in Dundas, Stormont and Glengarry counties, Eastern Ontario (KEELE, COLE) 19.

21—FUELS, GAS, TAR AND COKE

Constitution of coal. SHIGERŌ IWASAKI. *J. Chem. Ind. (Japan)* 23, 776-82 (1920).—In order to make proper use of the coal, not only as fuel, but also as raw materials for a manufg. industry, further study of its chem. and physical constitution is necessary. In physical examn., there are 3 methods: Microscopic examn. of a thin slice of the coal by transmitted light, examn. of polished surface by reflective microscopes, and X-ray examn. of a thin slice. The results of such physical analysis on certain Japanese coals are given and discussed. S. T.

Nature of coal. J. E. HACKFORD. *Mining & Met.* 163, No. 35-6 (1920).—The results of expts. on petroleum and derived bitumens bear on the nature and origin of coal and of petroleum. Studies of exts. obtained from coal by solvents and of the products of distn. of coal at low temps. have shown paraffins, olefins and naphthenes to exist in the coal. Coal tars are decompn. products of tars first formed at lower temps. Cellulosic constituents of coal form phenols when distd. Coal must have been formed at a temp. considerably below 300°. Coal was formed by the decompn. of buried terrestrial vegetation. Gas and oil are formed and the oil is held in the cellulosic sponge while decompn. proceeds. Even at 100° kerotenes are formed and remain as solids in the cellulosic structure. Petroleum is formed by the decompn. under certain conditions of vegetal matter free from cellulose. JAS. O. HANDY

Distribution of mineral matter in coal. R. LESSING. *Iron and Coal Trades Rev.* 102, 129-30 (1921); cf. *C. A.* 15, 1888-9.—Expts. were made of sepg. dirt from clean coal in samples of slack by elutriation by treating it in an upward current of water instead of by the float-and-sink method. The dust was first removed by using a current of low velocity and then the dirt by increasing the velocity so as to make the coal overflow and the dirt remain behind. The ash content of the dust thus collected varied from 18.98 to 24.68%, of the coal 1.44 to 1.98 and of the dirt 28.95 to 54.69%. The sp. gr. of the clean coal is low, av. of 1.289. This, together with the low ash content, shows the clean coal to be practically clarain and vitrain. The dirt from one sample, actually subdivided into a light, medium and heavy portion, showed ash contents, resp., of 6.33, 15.72 and 57.87%. The ash contributed to the entire sample by the dust was at least equal to, and in some cases more than twice as much as that contributed by the whole hulk of the clean coal, although the dust portion itself only ranged from 6 to 9% of the hulk of the sample. Some of the ash was sepd. into water-sol., acid-sol., and acid-insol. portions and each of these analyzed. The water-sol. portion of the ash from the dust of a Staffordshire slack amounted to 2.44%, from the clean coal 0.0, and from the dirt 3.70%; the acid-sol. portion from the dust was 23.72%, from the clean coal 50.5, and from the dirt 38.96; the acid-insol. portion from the dust was 73.84%, from the clean coal 46.02, and from the dirt 57.34. In order to find out if the different sizes composing each portion of a coal sample contain different % of ash, a Hamstead coal was crushed and ground to $\frac{1}{4}$ in. and divided into dust, clean coal ($D < 1.35$, vitrain and clarain, and $D > 1.35 < 1.5$, durain) and dirt, and these portions were analyzed. It was found that the ash in light clean coal (vitrain and clarain) decreases with size down to 30-mesh, with an increase in the portion through 30-mesh, while the durain portion shows a decrease down to 20-mesh, followed by an increase in the smaller size. The ash in the dirt consistently increased with decreasing size. The color of the vitrain fraction becomes darker, due to Fe and Mn, as the size becomes smaller, but the "through 30" portion is again as light as the dust, and, therefore, rich in fusain ash. The middle portion is fairly uniform in color, and apparently consists of the clay substance found in the durain from this coal. The dirt portion consists in the larger sizes entirely of Fe_2O_3 from pyrites, and in the smaller sizes of an increasing amt. of partings causing the increase

in the ash figures. Whenever L. uses the float-and-sink method, he adopts CCl_4 or a mixt. of this and petroleum ether.

J. L. WILEY

Committee for fuel utilization. WALCKENAER AND LANCKENON. *Bull. soc. encour. ind. nat.* 133, 124-5(1921).—The French Government, in connection with its Dept. of Public Works, has organized a Committee for the purpose of studying the better utilization of fuels and to institute measures for greater economy and better distribution of the same. Three sub-committees are appointed: the 1st has jurisdiction over fuels used in steam engines, the 2nd those in metallurgy and in industries employing furnaces, and the 3rd, inventions and special processes for carbonization and use of pulverized coal. Utilization of wood as an industrial fuel. Report of 2nd Sub-committee. CORNU-THERNARD and METAYER. *Ibid.* 126-35.—The French forests produce sufficient firewood yearly to supply a considerable demand for industrial fuel by careful regulation. In 1912, various sources produced 40 million stères (cu. m.). After air-drying a stère of hard wood weighs 500 kg., of soft wood 350 kg., 4-5 stères of the former and 6-7 of the latter being equiv. in heat value to 1 ton of coal of 7000 cal. In addition the ash content of 1-4% contains 15-16% of sol. alkali salts, 85-90% being in the form of carbonates of K and Na. There can be recovered then per ton of wood about 25 kg. of fertilizer titrating 9% of K_2O or an av. of 3.5 kg. of alk. carbonates. On the other hand, if the wood is carbonized there will be obtained approx. 25-27% charcoal, water, etc., 45-50%, tar 6-8% and gas 19-20%. The yield of by-products such as AcOH and MeOH is considerable. The charcoal makes excellent fuel for gas producers and also for domestic use. Raw wood has already been used quite extensively for firing boilers and making producer gas for steel furnaces. The Firminy Co. has been using it for the past year entirely in connection with Martin furnaces, about 700 kg. per ton of ingots produced, and with satisfactory results. The Neuves-Maisons Co. likewise use the same process except that they mix a small amt. of coke; 625 kg. of wood and 26 kg. of coke per ton of metal are consumed. The gas has the following compn.: CO_2 6.6%, CO 23.2%, CH_4 3.3%, H 11.9%. The operation of the furnace is in nowise changed. The use of wood for such purposes will be found very practical for plants in close proximity to the source of supply where transportation costs are negligible.

J. L. WILEY

Fuel economy. W. A. BONE, et al. *Rept. Brit. Assoc. Advancement of Science* 1920, 248-60.—See C. A. 14, 3144, 3310.

J. L. W.

Coal economy. GERALD LIGHTFOOT. *Sci. Ind. (Australia)* 2, 539-48(1920).—A general review of this subject, with special reference to the work which has been done in England and the U. S., under the headings: Destructive distn. of coal, low-temp. carbonization, use of powdered coal and domestic heating. In Australia 1,500,000 tons of coal or $\frac{1}{4}$ of the total amt. used is at present "carbonized;" 900,000 tons in gas works and 600,000 tons in coke ovens. In these processes the by-products are largely wasted.

G. W. STRATTON

Substitutes for coal—wood, peat, lignite. EMILIO DAMOUR. *Chimie et industrie* 5, 11-7(1921).—The main characteristic common to wood, peat, and lignite, is their high content of moisture or combined H_2O , which may reach 85-90% in the case of freshly extd. peat. This greatly decreases the "industrial calorific value" (defined as the calorific value obtained by means of a const.-pressure bomb calorimeter in which the air is introduced at 15° and the products of combustion are taken out at 100°; so that in many cases under ordinary conditions it is not possible to obtain more than 40% of the utilizable energy of the fuel. The most obvious remedy is to dry the material. This is relatively easy in the case of wood, and results in a saving of 10-5%. In the case of peat drying may be accomplished either by heat or by pressure; but the problem has not yet been completely solved from a com. point of view. Lignites are the most

difficult to dry, because they have a tendency to crumble and must then be burned pulverized or briquetted. The material, after having been air-dried to a content of 40-5% H_2O , can be treated in a gas-producer, the H_2O vapor in the gas being removed by condensation in a scrubber. This process was used for a steel furnace heated by means of gas from a producer fired with sawdust and wood waste (*Bulletin de l'Industrie Minière*, 1867, presented at the Universal Exposition, Swedish Section). In this case a large part of the heat is lost by the cooling of the gas; but this loss may be reduced by heating the primary air by means of these gases before cooling them. By means of a double combustion producer (Riché, Stockport etc.) a gas having a calorific value of 1000-1200 cal. and containing only traces of H_2O and no tar, is obtained. The only drawback to this process lies in the use of a H_2O -free fuel for the secondary combustion, the consumption of this fuel being proportional to the H_2O content of the primary fuel. Though the problem of the utilization of these lower-grade fuels cannot be considered as completely solved, very appreciable progress has been made, and several plants in France are now working quite satisfactorily without any coal. By combining scientific forestry and cutting methods with modern furnace equipment the saving effected can be raised from 10-5% to 40-50%.

The lignite mines of Collazzone (Umbria). B. LOTTI. *Rass. min. mel. chim.* 53, 21-2(1920).—These mines are located largely on the borders of the ancient Tiber lake in deposits of Pliocene age. The lignite is of good quality as shown by the analysis: Moisture 18.70%, ash 2.68%, fixed C 18.41%, volatile carbonaceous matter 60.21%, calorific value (dried) 5555 cal., total S 2.26%. The deposits are of considerable area and are promising.

Mine dusts: sampling, testing and treatment. W. H. McMILAN. *Iron Coal Trades Rev.* 102, 345-6(1921).—A lecture.

The formation of soot and sulfur compounds during the combustion of coal in boiler-furnaces. ED. DONATH. Brün. *Brennstoff Chem.* 2, 28-8(1921).—The soot formed during careless firing of furnaces is not pure amorphous carbon, but contains hydrocarbons (some sol. in C_6H_6) and S and N. High-S coals give chiefly H_2S when freshly fired; if this burns completely it is without action on the tubes unless it cools to a point where with H_2O and excess air it forms H_2SO_4 , in which case deposits of $FeSO_4$ and $Fe_2(SO_4)_3$ are formed. If H_2S is not completely burned it acts directly on iron at a temp. of 250-300°, forming deposits of FeS . The N content is often found partly in incrustations of $(NH_4)_2SO_4$ mixed with $FeSO_4$. Corrosion difficulties may be partly overcome by mixing with the coal 2-3% CaO or iron oxides. (Cf. C. A. 9, 3349.)

The nature of flame movement in a closed cylinder. C. A. WOODBURY, H. A. LEWIS AND A. T. CANLY. *J. Soc. Autom. Eng.* 8, 209-19(1921).—Flame propagation was studied by a photographic method. Mixtures of varying proportions of C_2H_2 , O_2 and N_2 and of H_2O -air were studied. In the case of C_2H_2 -air mixtures, ignited at atmospheric temp. and pressure, the max. velocity of flame movement is obtained with that mixture corresponding closely to the theoretical proportion for the formation of CO . Within the limits of the expts. carried out, it was found that increased temp. and pressure had little effect on the rate of flame propagation. A theory is advanced that auto-ignition of the high density gases ahead of the flame front is accountable for the fuel knock.

Formation of poisonous gases by certain forms of gas-fired water heaters. E. P. SCHUCH. Univ. Texas. *Am. Gas Assoc. Monthly* 3, 131-42(1921).—It is shown that gas-fired water heaters in which the flames touch the water vessels may produce enough poisonous gas to be harmful and even fatal. Hence such heaters should never be installed and operated without being connected to a flue. Expts. were made on a type of instantaneous water heater, as is often used in bathrooms, where the flame touches

extensively upon the metal surface and is cooled thereby below the ignition points of the gases, thus allowing them to escape unburned. The amount of CO formed is somewhat proportional to the areas touched by the flames. The rate of formation of CO is increased also by the variation in the draft of the heater, and by the increase in supersat. of the air with moisture.

J. L. WILEY

Carbon monoxide poisoning from the use of petrol engines—some experiences during the war. D. DALE LOGAN. *J. State Med.* 28, 306-10 (1920).—In air compressors, overheating of the compressor cylinder may decompose the lubricating oil with the production of CO and CO₂; and these gases then contaminate the compressed air, and form a source of danger to the workers in mine galleries who depend on the compressed air for their supply of air. Lubricants of low flashpoint should not be used in such app. The exhaust gases from gasoline engines, which were used for power purposes in dug-outs, gave rise to cases of gassing unless the exhaust was completely removed to the surface of the earth. Entrance of the exhaust gases into motor vehicles, especially their leakage into closed cars, produced cases of gas poisoning, and even death. The symptoms indicated CO as the poison; and expts. on white mice resulted in their death, their blood was satd. to a high degree with CO which apparently had found its way through the floor of the car. The compn. of the exhaust gases from gasoline engines is discussed.

JOSEPH S. HEPBURN

Both carbon dioxide and combustible gases in flue should be watched. OLOF RONGE. *Elec. World* 77, 712-3 (1921).—Brief discussion. C. G. F.

Ultimate boiler capacity limited by stoker conditions. J. HARRINGTON. *Elec. Rev.* 78, 452-4 (1921), 2 illus.—Discusses: size and distribution of air opening through grates; forced draft required to overcome resistance in fuel bed; formation of clinker influenced by character of coal and other factors. C. G. F.

The extraction of montan wax from lignite. Eo. DONATH. *Brennstoff Chem.* 2, 28 (1921); cf. C. A. 13, 744.—D. admits the priority of D. R. P. 325,165, Jan. 25, 1919, as disclosing the advantages of extracting montan wax with Me₂CO. W. B. V.

Simplex water-gas plant at Budleigh Salterton. J. W. GIMSON. *Gas World* 74, 163 (1921); *Gas. J.* 153, 543 (1921); cf. C. A. 14, 612.—For the year 1920 the av. make of gas per ton of coal was 18512 cu. ft.; during Jan. of 1921, 19300 cu. ft. A saving of 33% in coal. The blue gas is 340 B. t. u. and analyzes CO₂ and H₂S 4.9%, O₂ 0.2, unsatd. hydrocarbons 0.4, CO 48.0, CH₄ 7.5, H₂ 33.7, N₂ 5.3. Gas tar is used for enrichment, approx. 75% of that used being recovered as dehydrated tar. The mixed coal and blue gas (40%) gives 460 B. t. u. The fuel consumption is approx. 35 lbs. per 1000 cu. ft. of gas. The make of gas per ton of coke is approx. 65000 cu. ft. The av. cost of production of the water gas for 1920 was 1 s. 1¹/₄ d. per 1000 cu. ft.

J. L. WILEY

Evaluating water gas fuels. EDW. F. POHLMAN. *Gas Record* 19, No. 6, 39-40 (1921).—P. establishes a basis for comparing the relative values of generator fuels by using an av. analysis and an empirical formula based upon known qualifications of good generator fuel and av. operating results for a certain definite period of time (a year). The factors considered are: (1) % fixed C deficiency = 100 — %C; (2) % fuel consumption for evapn. of moisture = 8 × % of moisture; (3) % fuel unrecoverable in clinkers = 20 × % of ash; (4) % fuel loss due to effect of ash and cleaning time = 1.16 × % of ash; (5) credit due to release of volatile matter = $\frac{1}{4}$ of the volatile matter. Thus the relative value of a generator fuel analyzing moisture 1.8% volatile matter 3.55, fixed C 88.13, and ash 6.64 = $\frac{100 - 11.87}{1.33} - 7.20 + 1.18 = 19.85$ or 80.15%. Then the amt. of x fuel required to make 1000 cu. ft. of gas = $\frac{\text{required amt. of standard fuel} \times \text{its relative value}}{\text{the relative value of } x}$. Figures thus obtained agree very closely with those obtained in actual practice.

J. L. WILEY

Water gas challenges producer gas. B. M. HERR. Combustion; *Gas Age* 47, 189-90(1921).—H. compares the B. t. u. furnace efficiency of natural gas, water gas and producer gas at prescribed temps. To keep the furnace at a temp. of 560° F. for a certain period, the amts. of the 2nd and 3rd necessary to replace 100 cu. ft. of the 1st are resp., 301 and 834 cu. ft.; the amts. of the latter required for higher temps. increasing rapidly for increase of temp. and of the 2nd diminishing very slightly. At established prices for the 3 gases, producer gas is the most economical below 1400° F., while from this point water gas shows a considerable economy, this increasing with increase of temp.

J. L. WILEY

Gas-producer plants with recovery of crude tar. E. ROSER. *Z. Ver. deut. Ing.* 64, 857-63(1920).—Great stress is being put in Germany on the total gasification of coal, the recovery of the crude tar, the distn. of these tars into their fractional components, notably the large amts. of fuel oils, and the use of the cold gas in metallurgical operations and internal-combustion engines and gas turbines for production of power. The *Thyssen gas producer*, built on somewhat similar lines to the Mond producer, is the app. which is bringing to the gas industry a special prominence. Crude-tar recovery has become of considerable financial importance as well as an economic fact. Returns from the tar per ton of coal has increased about 3 fold and the amt. which it is possible to recover from the coal and lignite gasified will tend to make Germany independent of foreign oil supplies, besides giving a very cheap source of energy. Recoveries of from 25 and 30 kg. of water-free tar to 75 kg. per ton of coal are reported, together with around 40 kg. of $(\text{NH}_4)_2\text{SO}_4$. A noteworthy point is the high yield of fuel oils from producer tars and also their high paraffin content, as high as 50% or more of oils and 2% of paraffins. The gas yield according to the kind of coal ranges from about 2.5 to 4.75 cu. m. per kg. of coal with a sensible heating value of from 1140 kg. cal. with recovery of by-products to 1620 kg. cal. without recovery and from 1338 to 1710 kg. cal. resp., with lignite briquets. The flame temps. in the above cases are resp., 1310 to 1526 and 1525 to 1665 with air at 20°. By heating the air to 1400° and the gas to 1250° an increase of only about $\frac{1}{3}$ is obtained. Development of the industry in this direction and toward increasing the efficiency of recovery and utilization is proceeding.

J. L. WILEY

Crude-tar recovery in the gas producer. H. R. TRENNLER. *Z. Ver. deut. Ing.* 64, 997-1002(1920), 5 figs.—T. discusses crude-tar recovery through coal distillation in revolving retorts (Roser, *C. A.* 14, 2699) and through complete gasification in the Thyssen gas producer (cf. preceding abst.) and by means of double-gas and trigas installations (cf. Pott and Dolinsky, *C. A.* 14, 1028; Strache, *C. A.* 14, 1891, 2699).

J. L. WILEY

Gas industry on the heat-unit basis. VII. The new act from the secretarial point of view. T. P. RIDLEY. *Gas J.* 153, 396-7(1921). VIII. Gas regulation act from an industrial heating point of view. C. M. WALTER. *Ibid.* 464-5. IX. Gas regulation act from the chemical standpoint. E. W. SMITH. *Ibid.* 532-3.—Every gas plant should have a trained chemist to look after the control testing, supervise distinctly chem. processes, and undertake technical research. A scheme is proposed for standardizing and coordinating control testing throughout the country. X. Calorimetry and the gas regulation act. JOHN F. SIMMANCE. *Ibid.* 607-8.—No recording calorimeter can be relied upon to be more accurate than within 1.5% of the total heat value of the gas. XI. Why I abandoned the sliding scale. CHAS. CARPENTER. *Ibid.* 671-2.

J. L. WILEY

Industrial gas requirements. ANON. *Gas Age* 47, 253-6(1921); *Gas Record* 19, No. 6, 43-6(1921).—Rules and data have been worked out for detg. gas requirements for 10 classes of industrial equipment as follows: Heating water, steam boilers, varnish

burners, coffee roasters, core baking, japanning, galvanizing, soft metal melting, brass melting and oven furnaces.

J. L. W.

Addition of carbon dioxide in the generator process. Gwosdz. *Feuerungs-technik* 9, 73-44(1921).—Review of the work of Essich, Tait and others.

C. J. West

Producer gas dust arrester. W. H. SPEAR. *Gas Age* 47, 187-9(1921), 2 figs.

The producer fuel used is coke passing through a $1\frac{1}{4}$ in. screen. Due to the high-blast pressure necessary to burn this, considerable dust is carried along with the producer gas. The first 50% of this dust is removed at a dust trap in each individual producer flue; 48% in a cyclone arrester installed in the main gas flue header, and 2% in 8 dust traps distributed along the header. There is also a dust trap located directly under the gas damper on the intake flue to each bench, but only a very small amt. of dust settles therein. This system is very efficient as shown by the fact that heat conditions have not changed in any respect since the plant began operation.

J. L. WILEY

Composition of coal gas in relation to its utilization. R. V. WHEELER. *Sheffield Univ. Gas J.* 153, 815-18(1921), 4 charts.—The lecture shows 2 things: The limits within which variations in the proportion of combustible constituents affect the behavior of coal gas on burning; and what is the effect of the incombustible constituents. The conclusions are drawn from known scientific facts, and are based upon the speed of the propagation of flame in the mixt. of gas and air issuing from a bunsen burner, which propagation of flame varies with the compn. of the mixt. and the nature of the combustible gases and also determines the character of the flame. W. argues that there should be no limitation of combustibles in the gas; if there is to be any it should be in the H, as this gas is more difficult to control. The addition of CO to CH₄ and H has little effect on the speed of propagation of flame, but it widens the range of inflammability and, therefore, gives greater adaptability to the gas. Also, in general, a mixt. containing CO, CH₄ and H in equal proportions is most suitable for all Bunsen-burner work. From curves it is shown that for a given pressure of gas at the burner, the use of CH₄ alone would permit a high degree of primary aeration, but would give only a small range of adjustment; the use of CO alone allows of a high degree of primary aeration and a wide range of adjustment, whereas H alone would permit of hardly any primary aeration and, therefore, a low degree of calorific intensity. The greater the amount of primary air, the smaller the amount of secondary air to effect complete combustion. Assuming a constant speed of the mixture of 150 cm. per sec., with a straight coal gas only 1.5% of gas requires burning by secondary air, with water gas 16% must be so burned. In ordinary app. designed for straight coal gas, 50% of coal gas and 50% of water gas is about the limit for water gas, and this mixt. is very serviceable despite its low calorific power. There is no reason for trying to limit the proportions of combustible gases present in town gas. Regarding incombustibles, the calorific efficiency of a fully aerated mixt. is not affected very much by even a proportion of 30%. What incombustibles do is to reduce the margin of adjustability, meaning that slight variations in pressure will cause wide fluctuations in the character of the flame and in the distribution of heat throughout it, with consequent inefficiency of the furnace.

J. L. WILEY

Erection of a setting of Glover-West retorts. A. ST. D. CORDER. *Gas J.* 153, 540-1(1921); *Gas World* 74, 191-2(1921).—Description of a plant at Bridgewater.

J. L. WILEY

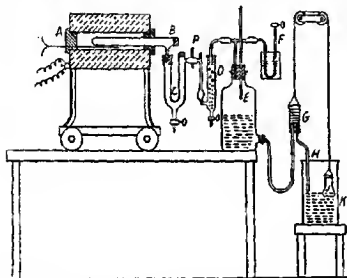
Some industrial uses of gas. J. H. BRODIN. *Soc. Tech. Gaz. Gas J.* 153, 544-5(1921).—B. describes the application of gas-heating to recovery of wood from cotton-wool mixts., mining of machine gun-bands, and tempering and case-hardening of metals.

J. L. W.

Gas ovens for small plants. A. MACARTHUR. *Gas Age* 47, 229-33(1921); *Gas Record* 19, No. 6, 27-8, 49(1921).—Details are given of a by-product regenerative combination gas oven designed for small plants and giving the advantages of coke ovens. In principle it is a shortened coke oven operated in the same manner and fired with producer gas.

J. L. WILBY

Assay of coal for carbonization purposes. T. GRAY AND J. G. KING. *Iron and Coal Trades Rev.* 102, 362(1921).—In Tech. Paper No. 1 issued by the Fuel Research Board of the Dept. of Scientific and Industrial Research details are given of exptl. work in connection with a method of coal assay to ascertain by direct weighing and measurement, and with a precision not hitherto attained, the yields of gas, oil, water and carbonaceous residue resulting from the carbonization of coal at definite temps. The app. is shown in the cut. *A* is a nichrome-wound elec. furnace, its temp. regulated by a thermocouple attached to the outside of the silica tube *B* at the middle of the furnace. The U-tube *C* acts as a condenser. *D* is filled with glass beads drenched with H_2SO_4 for absorbing the NH_3 . The gasholder *E*, filled with a mixt. of glycerol and water,



an almost satd. aq. soln. of $MgCl_2$, or water satd. with coal gas from a previous expt., is connected to a glass reservoir *G* by means of a rubber tube; this reservoir is suspended over a pulley counterbalanced by an adjustable wt. As gas enters *E* the displaced liquid passes into *G* and overflows into *K* in which the counterweight *J* floats. If *E* and *K* have the same diam., a fall of level in the former causes an equal rise in the latter, and the movement of the

float *J* lowers *G* to the same extent, thus maintaining a const. pressure in *E*. Any desired difference of level may be maintained by adjusting the height of *K* or of the pulleys. The coal sample is ground to 60 mesh and dried at $105-110^\circ$. The gasholder is filled up to the stopper, the height of the reservoir *G* is adjusted and the clean U-tube *C* is weighed and attached. The tube *B*, with a plug of asbestos wool, is weighed to the nearest cg. and is charged with 20 g. of dry coal spread out evenly. The charged tube is then connected to *C* and the furnace previously heated to 300° is pushed into position. As soon as the evolution of gas ceases, the temp. is raised gradually to $550-600^\circ$ in 1 hr. Observations are made of the temps. at which water and oil appear. After 1 hour of heating at the above temp., the pinchcock *P* is closed, *B* is opened and the furnace withdrawn. The yield of coke is arrived at by weighing *B* when cold. From the increase of wt. of *C*, the total yield of oil and water is obtained and the vol. of the aqueous portion is measured by washing the contents into a 10-cc. graduated cylinder with $CHCl_3$. The contents of *D* are washed into a flask, mixed with the aqueous washings from *C* and distd. to give the yield of NH_3 and bases. To ascertain the gas vol., water is removed from *K* by means of a pipet, and is allowed to flow into *G* which is gradually raised till the top of the inlet is on the level of the liquid in *E* and the liquid in *F* is at a level gage, any unused water being returned to *K*. From the wt. and the sp. gr. of the liquid in *K* the vol. of gas may be calcd. at the prevailing temp. and pressure. If a gas free from air is desired, a second test should be run, first forcing the gas in *E* back through *B* to drive all air out of the app. To test the method, 2 series of distns. were carried out at each 550° and 600° . The av. results in g. per 100 g. of coal were as follows: At 550° —coke 75.75, oils 13.75, liquor 2.97 cc., gas 7.11;

gas satd. at 30 in. and 60° F. 8400 cc.; sp. gr. of gas 0.695. At 600°—coke 74.13, oils 14, liquor 3.25 cc., gas 8.44 (10510 cc.); sp. gr. 0.86. The max. variation between the results for each of the temps. was so small that the method appears very satisfactory. Also in *Gas J.* 153, 740-1(1921); *Chem. Trade J.* 68, 409-10(1921).

J. L. WILEY

Alcohol from coke-oven gas. CECIL F. TIDMAN. *Iron and Coal Trades Rev.* 102, 350(1921); cf. *C. A.* 14, 826.—To effect an economical fixation of C_6H_6 , it has been found that time and some form of mechanical agitation are necessary. In a lab. test with 3 min. of agitation at a temp. of 80°, 80-90% absorption was effected. Such a process also cuts down considerably the amt. of scrubbing plant necessary. In recovering the alc. from the acid, distn. under reduced pressure was found to be effective and prevented frothing. Two impurities were found in the by-product alc. and isolated, an oil supposed to be a condensed hydrocarbon oil and a crystal substance with compn. C 40%, H 6.6 and S 53.4. It was fixed as diethylene disulfide synthetically produced from reaction of S in the gas with the C_6H_6 at the expense of alc. Therefore, care must be taken to have a perfectly pure gas. The H_2S has been completely removed from the gas by scrubbing with a soln. of SO_2 in excess, this excess being later removed by scrubbing with water. Tests were made on a 4-h. p. motorcycle as follows: 90% alc. used in mixts. with motor benzene: No. 1 shell spirit 64.6 mi. per gal.; 50% alcohol and 50% benzene 78.5 mi.; 75% alcohol and 25% benzene 74 mi.; with alc. alone 58 mi.

J. L. WILEY

Hydraulic mains and ascension pipes. THOS. JOHNSON, *Gas World* 74, No. 1911 (Coking and By-Products Sec.), 13-17(1921).—J. does not agree with Foxwell (*C. A.* 15, 1068) that ascension pipes should be placed at the end of the ovens, but rather the center position is most advantageous, since there is not so much chance for decomposition of the gases. The design of ascension pipes and hydraulic mains is discussed.

J. L. WILEY

Condensation and compression. J. W. LANSLEY. *Gas Age* 47, 191-2(1921).—Losses through high pressure and low temps. in gas distribution are discussed. The max. possible condensation loss occurring in illuminants amts. to 1.27% of the high pressure send-out, considering the following conditions: Barometer 29.5 in., holder pressure 0.8 in., temp. of gas leaving holder 70° F., temp. of gas in mains 58° F., and pressure in mains 43 lbs.

J. L. W.

The water-vapor content of technical gases. G. SAILER. *Feuerungstechnik* 9, 88-9(1921).—S. discusses the method of calcg. the H_2O -vapor content of tech. gases of 1 cc. or in vol.-%, also the effect of the H_2O content upon the energy value of the gases. He points out that it is impossible to compare 2 gases without knowing the H_2O content, which is often not given in the original analysis.

C. J. WEST

The gasification of wood and wood-wastes in gas-producers. GWOSDZ. *Brennstoff Chem.* 2, 21-3(1921).—A review of various attempts to utilize wood in gas-producers and a description of the Deutz and Pintsch producers designed for that purpose.

W. B. V.

Distillation of lignite at low temperatures. E. SANNA. *Rass. min. mel. chim.* 53, 81-2(1920).—Distn. of lignite at 450° yielded per kg. 300 l. of gas of calorific value 1500 cal., 700 g. fine coke suitable for domestic use when briquetted, and 15 g. tar. Distn. of lignite at high temps. in coke ovens or producers is unsatisfactory on account of the formation of sulfurous gases and a fusible ash.

J. S. LAIRD

Low-temperature tars: their preparation and economic importance. FRITZ FRANK. *Chem. Ind.* 43, 387-92(1920).—Low-temp. coking of coal, lignite, peat, etc., furnishes a tar not unlike crude petroleum, and quite different from ordinary coal tar. To supply war needs for lubricants and fuel-oils in Germany this low-temp. coking, hitherto

of only scientific interest, was carried out on a commercial scale. The most successful method consisted in passing hot generator gas through a layer of the coal, either lying directly on the fuel bed, or, retort-like, in the combustion chamber, but sepd. from the burning fuel. Stirring aided in the coking, and rotary kilns gave excellent results. The tar was sepd. from the gas in the ordinary manner, and the gas, dried and freed from dust if necessary, was found very satisfactory for fuel, particularly for glass furnaces. The tar, consisting of paraffins, olefins, and naphthenes, with small quantities of aromatic hydrocarbons and phenols, was distd. as rapidly as possible with superheated steam in a very high vacuum; the non-volatile residue was either used as pitch or destructively distd., yielding light hydrocarbons, cryst. paraffins, and small quantities of phenols. The combined distillates were freed from solid paraffins and redistd. as before, sepg. the oil into the desired fractions.

DONALD W. MACARDLE

Wood-tar oils suitable for motors. EVERETT NORLIN. *Teknisk Tidskrift (Vehuppblg.)* 50, 4-13(1920).—A detailed résumé of the subject, comparing the wood-tar oils with the usual liquid fuels. The article contains 12 tables and 5 curves.

A. R. ROSE

Rapid determination of water in tar emulsions. W. W. ODELL AND E. W. THIRLE. *Am. Gas J.* 114, 252, 257-8(1921); *Gas Record* 19, No. 6, 29-30(1921); *Gas Age* 47, 234-5(1921).—Aside from the various modifications of the distn. methods, 2 methods have been used to det. water in tar. Brunkow (*C. A.* 10, 2398) evapd. it in a drying oven, while Kayser used a calcium carbide method. The standard method is that of distn. In the Barrett Co. method 200 cc. of the emulsion are mixed with 200 cc. of light oils and distd. to 400° F., the water being collected and measured. An accuracy of 0.1% is claimed. There is also a method used in connection with petroleum emulsions by adding to them a light gasoline and centrifuging (Allen and Jacobs, *Bur. of Mines, Tech. Paper* 25). The first of the 2 methods described here is similar in principle. Ten g. of the tar emulsion are weighed into a cream-testing bottle (a hottle with a long slender neck graduated in fractional parts of a cc.) and CCl_4 is added up to the top graduation. It is then centrifuged for 2 or 3 minutes at 2000 r.p.m. and the number of divisions read off occupied by the water and the sludge, taking as the upper mark a point half-way between the top and bottom of the upper meniscus. Twice the number of divisions equals the % of water by wt. If % by vol. is desired take 10 cc. of emulsion instead of 10 g. The method for large amts. of water is accurate within 1%. It is more accurate the smaller the amt. of water in the emulsion. Eight detns. can be made and the app. cleaned in half an hour. Method 2 depends upon the strong absorbing power of carbon black for the oils of which tars are composed. One hundred g. of the emulsion are weighed into a mortar, and successive small portions of carbon black are added, and mixed well with a spatula until the residue becomes a thick paste and no more water separates. The cc. of water sepd. is the real water content of the emulsion. By allowing 2% of the % of anhydrous tar for the water absorbed by the carbon black, results very close to the true value are obtained. This method is best suited to emulsions of high water content.

J. L. WILBY

Gravimetric estimation of creosote. A. LAZAR. *Gas J.* 153, 622(1921).—The approx. creosote content of the tar oil is first detd. by the "difference method." An amt. of 25 g. of the oil, weighed out exactly to 0.1 g., is extd. 3 times in a sepg. funnel with the calcd. amount of 5% of NaOH solution. The alk. washings are then extd. twice with ether. The oil-free sodium cresylate soln. is decompd. with dil. H_2SO_4 and the pure creosote thus liberated is extd. by 2 or 3 shakings with ether. The combined ether exts. are dried by means of anhydrous Na_2SO_4 . A 50-cc. distn. flask, containing a little porous earthenware, is weighed to 0.4 g. and a dropping-funnel adjusted to a tightly fitting stopper. The dried etherial soln. is filtered into the funnel, and the flask warmed

on a water bath to drive off the ether. The filter and the funnel are washed with ether and the washings added to the flask. When nothing further distills over, the condenser is removed and a test-tube secured to the outlet tube. The funnel is replaced by a thermometer which dips into the liquid. By heating with a small hunsen flame, the temp. is raised to 50°. The thermometer is then raised to the usual distn. position and the heating continued until the creosote vapors arrive at the bulb of the thermometer. At this point all of the solvent will have been driven off and none of the creosote lost. The flame is removed, the flask allowed to cool and then weighed. The method gives the true content of creosote with great accuracy and permits of the recovery of the greater part of the ether used.

J. L. WILEY

Steam in fractional distillation (SHAW) 13. Indicators for carbon dioxide and oxygen in air and flue gas (MILLIGAN, *et al.*) 1. Catalysis in industrial chemistry (RIDGAL) 13. Fermentation of cellulose (gas production) (FOWLER) 16. Analysis of ammonium sulfate (LOWE) 7. Helium (MOORE) 2. Determination of small quantities of carbon monoxide in the air and in smoke (FLORENTIN, VANDENBERGER) 7.

Retort oven for coking coal. H. KOPPERS. U. S. 1,369,673, Feb. 22.

Dewatering peat. A. TENBOSCH. U. S. 1,369,611, Feb. 22. Peat is introduced into a vertical column of such height that the wt. of the peat on the lower portion of the material in the column is so great as to express a portion of the H₂O, which is drawn off through a filtering device. After this preliminary sepn. of H₂O, a further quantity of H₂O is removed by subjecting the material in the column to the action of steam and pressure.

22—PETROLEUM, ASPHALT AND WOOD PRODUCTS

F. M. ROGERS

Colloid chemistry in petroleum. A. E. DUNSTAN. Third rept. on colloid chemistry, Brit. Assoc. (1920). A review. JEROME ALEXANDER.

America's petroleum problem. J. O. LEWIS. *J. Franklin Inst.* 191, 357-79 (1921).—An outline is given of the American petroleum industry. The sources of domestic supply and the total crude oil supply of the world are enumerated. In conclusion, an account is given of the various ways in which the domestic supply may be so increased as to meet the growing demand. JOSEPH S. HEPBURN

Saybolt "furol" viscosimeter. E. W. DEAN. Bur. of Mines, *Reports of Investigations* No. 2215(1920).—For the purchase of petroleum fuel oils the specification of the sp. gr. of the oil does not give a true index of its quality, and the only available viscosimeter, the Redwood admiralty instrument, was difficult to obtain and use. It was found that by enlarging the bore of the efflux tube of the Saybolt universal viscosimeter so that the efflux time was reduced to about one-tenth, an instrument was obtained which was satisfactory for work with very viscous oils. For the past six months, instead of using the sp. gr. specification in the fuel oil contracts of the Shipping Board, a clause has been inserted to the effect that the oils shall have a maximum viscosity of 350 sec. at 122° F. (50° C.) with the new instrument. The ratio between the efflux times of the Saybolt "furol" viscosimeter and the Redwood admiralty instrument is expressed approx. by the equation: Saybolt "furol" efflux time = 1.17 × Redwood admiralty efflux time. The instrument, whose name was coined from the words "fuel and road oils," is at present for sale by at least one supply house.

DONALD W. MACARDLE

Petroleum industry. KAJIRŌ KONDŌ. *J. Chem. Ind. (Japan)* 23, 681-723 (1920).—A review of petroleum industry of the world is given. The past and present states of this industry in Japan are given in detail. In 1918 Japan produced only 0.48% of the total world's production, 40% of her own demands being met by import. Its relation to the national defense, activity of National Geological Survey, detailed processes used for collection, purification, its by-products, and phases of taxation and transportation problems are discussed. Complete tables for the amt. and the kind of the oil produced, and where and how they are used are given. S. T.

Properties and tests of fuel oils. R. PINTA. *Technique moderne* 12, 501-8 (1921).—Outline of the methods to be used in sampling, and detg. homogeneity, d., H_2O , dirt, distn. test, acidity, impurities removed by H_2SO_4 , asphalt, paraffin, ash, coke, ultimate compn. (C, H, O, N), calorific value, flash and burn points, solidification point, viscosity, together with a table giving the specifications of the French, British and American admiralities, of the U. S. Bur. of Mines, and of the "Société des Consommateurs de Pé-trole." A. P.-C.

Efficiency in the use of oil as fuel. W. N. BEST. *Mining & Met.* 163, 35 (1920).—The use of oil as boiler fuel in large mfg. establishments has the following advantages over coal firing. Labor cost is less. One man can fire and water-tend 12 300-h. p. boilers. Oil firing takes care of peak loads. Coal dust and ashes are eliminated. Oil is more cheaply delivered and distributed. Oil heavier than $20^\circ B\acute{e}$. should be heated by steam nearly to the vaporizing point. There should be accurate temp. measurement and control. The oil should be kept constantly circulating in the supply lines between pumps and burners. A pressure-relief valve at the end of the burner installation is necessary. An overflow pipe returns the unused oil to the supply tank. Oil burners are of 3 types—the external atomizing type, used for locomotive and stationary boilers and large furnaces; the internal atomizing type used for small furnaces; and the mechanical type used on ocean-going vessels and requiring no steam but only high pressure service through a small aperture. Burners which "carbonize" should be scrapped. They are wasteful and not dependable. Oil and steam orifices should be sep., thus avoiding high-pressure oil service and "cutting" by sand, etc., in oil. The burner flame should fill the combustion chamber. The oil orifice should be large enough for free movement of tar or heavy oil. The atomizer opening should be as small as may be. Jas. O. HANDY

The cracking of mineral oils. I. LAZENNEC. *L'age de fer* 36, 803-4 (1920).—Very brief outline of the first work done on cracking (1863-1887), of the theory of cracking, and of the processes used industrially. A. P.-C.

The refining of petroleum. I. LAZENNEC. *L'age de fer* 37, 857-9 (1921).—Very brief outline of the French, American and Russian processes for the distn. of petroleum, and of various methods for the chem. purification of the distillate. A. P.-C.

The by-products of petroleum. I. LAZENNEC. *L'age de fer* 37, 880-3 (1921).—Brief outline of the method of prepn., properties, and uses of vaseline and paraffin, of the purification, uses and detn. of naphthenic acids, of the use and merits of fuel oil, of the use of natural gas, and of the sepn. of He from natural gas. A. P.-C.

Perfect petroleum products. W. C. WELLS. *Railroad Red Book* 38, 472 (1921).—The use is urged of permanent gases in place of steam as an aid in the sepn. of the ingredients of petroleum. The amt. of heat required to transform 1 lb. of H_2O into dry steam (28.6 cu. ft.) at 212° will raise 29.67 lbs. CO_2 (equiv. to 350.17 cu. ft.) to $212^\circ F$. and this will have an absorptive capacity of 92,795 grains as compared with no absorptive capacity for steam which has received the same number of heat units. The sepn. of petroleum by means of heated permanent gas would give more efficient sepn., larger proportionate yields with a minimum of decompn. and loss.

R. L. SIBLEY

Absorption as applied to recovery of gasoline left in residual gas from compression plants. W. P. DYKEMA AND ROY O. NEAL. *Bur. of Mines, Tech. Paper 232*, 43 pp. (1920); cf. *C. A.* 13, 1142, 2588.—This paper deals with the recovery of gasoline by means of the absorption process from the residual gas of plants where motor fuel is obtained from natural gas by mechanical compression and cooling, the gasoline present in the natural gas being absorbed by oil and subsequently being distd. off, or being absorbed directly in naphtha. Large returns follow from a trivial plant cost.

JEROME ALEXANDER

Distillation of shale oil. JAMES A. BISHOP. *Mining Sci. Press* 120, 371-5 (1920).

—A semi-popular review.

JEROME ALEXANDER

Oil shale in Colorado. R. D. GEORGE. *Railroad Red Book* 38, 3, 457-61 (1921).

—The Green River shales lie the second from the bottom in the Eocene rock series. These shales occur in bands and strata ranging in thickness from a few in. to 75 or 80 ft. and differ widely in color, compn., sp. gr., hardness and brittleness.

R. L. SIBLEY

Possible uses for spent shale from oil-shale operations. KIRBY THOMAS. *Chem. Met. Eng.* 24, 389-90 (1921).—The disposal of spent shale is a serious economic as well as mechanical problem in many oil-shale operations. The content of fixed C (7% and more) suggests utilization as a fuel but a more promising outlet is as a material for making brick and tile. Spent shale can also be used in cement and may lead to coordinating shale operations with the cement industry.

S. D. KIRKPATRICK

Petroleum and asphalt in Venezuela. I and II. ARTHUR H. REDFIELD. *Eng. Mining J.* 111, 354-7, 393-5 (1921).—The geological features of the basin of Lake Maracaibo and of the shores of the Gulf of Paria are discussed. Production and supply statistics are given. The oil is asphaltic, having a sp. gr. of 0.928 to 1.02. Not more than 3% of naphtha and no more than 7% of kerosene have been obtained in refinery practice. The activities of the various companies interested in Venezuela are described. Bermudez asphalt is described briefly. A bibliography is appended.

W. F. FARAGHER

The colloidal state of matter in its relation to the asphalt industry. CLIFFORD RICHARDSON. *Third rept. on colloid chemistry, Brit. Assoc.* (1920)—A brief review.

JEROME ALEXANDER

"The chemist and the crude factory" in the hardwood distillation industry. R. E. GILMORE. *Canadian Chem. Met.* 5, 37-41 (1921).—G. has outlined briefly the position of the chemist in the industry, the raw material used and the crude products manufd. Factory operations (handling of cordwood raw material, destructive distn. proper; and treatment of pyroligneous acid liquor) are discussed, and a flow-chart of the distn. process according to Canadian practice is included. Methods now used in the analysis of crude furnished products are given briefly. Among the industrial research problems that deserve immediate attention are: Studies on proper carbonizing practice, utilization of hardwood tar and creosote oils and new uses for charcoal. More purely scientific problems also are outlined.

LOUIS E. WISE

Activation of wood-charcoal by heat-treatment. JAMES C. PHILIP, SYDNEY DUNNILL AND OLIVE WORKMAN. *J. Chem. Soc.* 117, 362-9 (1920); cf. *A. B. Lamb, et al., C. A.* 13, 1279.—On heating wood-charcoal *in vacuo* at temps. from about 800° and upward, its ability to adsorb SO₂ gas and methylene blue from aq. soln. is increased many times. O is retained by charcoal with great pertinacity and CO₂ is always formed on heating, even in a current of N. The view is advanced that heating results in the widening, by progressive oxidation, of the capillary channels with which the granules are riddled, so that although the external vol. is practically unaltered, its bulk is diminished and the effective surface enormously increased. In unactivated charcoal the

capillary mouths are easily blocked, and, therefore, its adsorption limit (as expts. showed) lies at a lower pressure than that of activated charcoal. The amt. of ash seems to exercise no influence on adsorption; and the decolorizing power appears to be primarily detd. by its physical structure and surface development. The efficiency of animal-charcoal itself is a function of the heat treatment it has received, and can be materially increased.

JEROME ALEXANDER

The manufacture of ethyl alcohol from wood waste (SHERRARD) 16. Nature of coal (HACKFORD) 21. Steam in fractional distillation (SHAW) 13. Viscosity tester (MALLISON) 1.

Dense charcoal. L. F. HAWLEY. U. S. 1,369,428, Feb. 22. Wood charcoal having a sp. gr. of at least 0.95 is made by comminuting wood, forming the wood into blocks, and subjecting the latter to a pressure of at least 30,000 lbs. per sq. in. and distg. the blocks under a directly applied mechanical pressure increasing from 50 lbs. per sq. in. to 120 lbs. per sq. in. and then decreasing through the same range in successive alternations.

23—CELLULOSE AND PAPER

A. D. LITTLE

Cellulose esters. FOSTER SPROXTON. *Third rept. on colloid chemistry, Brit. Assoc.* (1920).—A suggestive review. S. considers reasonable Dubosc's view of *celluloid* as a *camphrogel* of nitrocellulose.

JEROME ALEXANDER

New method for the production of cellulose acetate. W. LEIGH BARNETT. *J. Soc. Chem. Ind.* 40, 8-10T (1921).—By using a mixed catalyst of Cl and SO₂ (cf. Brit. Pat. 24,382 of 1910; *C. A.* 5, 3157), a satisfactory change of cellulose into the acetate is accomplished with the minimum amt. of change to the parent complex. Acetylation proceeds at any temp., and no special precautions are necessary. Filter paper, cotton wool and bleached and gray American cotton yarns were used successfully. The best method for isolating the ester from the AcOH was found to consist in the addition of CHCl₃ and AcMe followed by mixing with an excess of H₂O. When the volatile solvent is distd. off, the ester is gradually pptd., due to the rising of globules of the CHCl₃ soln. through the H₂O. The product depends upon the conditions of acetylation. Below 65° and with a trace of SO₂, the product is chiefly the *diacetate*. If the ratio of Cl to SO₂ is nearer unity the product is the *triacetate*, particularly if the temp. be allowed to rise above 65°. A typical expt. is: 5 g. filter paper immersed in 20 cc. glacial AcOH and 20 cc. Ac₂O containing 0.32 g. Cl, followed by 2 cc. Ac₂O containing 0.26 g. SO₂. In less than 5 min. soln. was complete. After a further 5 min. 20 cc. CHCl₃ were added and the ester was sepd. as usual. Filter paper acetylated more vigorously but cotton gave a soln. of better color and higher viscosity than the filter paper. The acetates may be analyzed by soln. in AcMe, hydrolyzing in the cold by shaking with standard NaOH, allowing to stand 1 day, dilg. with H₂O and titrating the excess of alkali. A correction must be made for the acidity of the acetone and for any decompn. of the cellulose.

C. J. WEST

Uses and methods of working acetylcellulose. GUSTAV BONWITT. *Charlottenburg. Chem.-Ztg.* 44, 973-4 (1920).—A general historical review of the cellulose acetate industry and a discussion of the principal uses of these esters. It contains no original material.

C. J. WEST

Recovering newsprint. CHARLES BASKERVILLE AND RESTON STEVENSON. *J. Ind. Eng. Chem.* 13, 213-4 (1921).—Newspapers are pulped with water containing 60

lbs. NaOH or 200 lbs. soda ash per ton of paper, to which are added 100 lbs. or more of American fuller's earth. The suspended material appears to remove the oils of the binder and also attracts C away from the pulp and holds it. The alkali and fuller's earth should be added to the H_2O and the mixt. beaten to 50° before the paper is added. The product, after thorough washing, can be bleached by the use of 20 lbs. SO_2 per ton of papers in the cold in 15 min. C. J. WEST

Regenerating bookstock. CHARLES BASKERVILLE AND C. M. JOYCE. College of the City of N. Y. *J. Ind. Eng. Chem.* 13, 214-5(1921).—Ten lbs. borax, 10 lbs. soap, 2 gal. kerosene and 2 gal. pine oil are used per ton of bookstock, in water to make a 3-6% pulp. Time is saved by beating the mixt. to 75-100°. The pulping requires 1 hr. or less, after which the pulp is thoroughly washed and bleached or tinted as desired (cf. C. A. 14, 3320). C. J. WEST

The reclaiming of acid. O. L. BERGER. *Paper* 27, No. 16, 22-3(1920).—See C. A. 15, 313. H. H. HARRISON

The estimation of mechanical wood pulp. M. G. KOTEBHASKER. *Paper Maker Brit. Paper Trade J.* 61, 63(1921).—A known quantity of pure mechanical wood pulp was covered over with a known vol. of standard *p*-nitroaniline soln. and after the absorption was complete the residual *p*-nitroaniline was estd. by means of $TiCl_3$. The absorption is a quant. reaction, air-dry mechanical wood pulp absorbing 56-57% of *p*-nitroaniline. On this basis several papers of known compn. were examd. and results were obtained correct to within 2% error. Calcns. were made on the basis of 1.5% allowance in the case of sized papers and 10% for the moisture. H. H. HARRISON

Standard specifications for cement and lime paper bags. PAUL L. HOUSTON. *Bur. Standards. Tech. Assoc. Papers* 3, No. 1, 7-11(1920).—See C. A. 14, 3319. C. J. W.

Use of sulfur in cooking soda pulp. GEORGE K. SPENCE. *Tech. Assoc. Papers* 3, No. 1, 14-6(1920).—See C. A. 14, 3319. C. J. W.

Substitutes for alum and rosin. W. E. BYRON BAKER. *Tech. Assoc. Papers* 3, No. 1, 16-7(1920).—See C. A. 14, 3319. C. J. W.

Continuous automatic mixing system for paper stock. EDWARD J. TRIMBEY. *Tech. Assoc. Papers* 3, No. 1, 21-3(1920).—See C. A. 14, 3319. C. J. W.

Substitutes for alum in papermaking. MAX CLINE. *Tech. Assoc. Papers* 3, No. 1, 17-18(1920).—The best remedy for the rosin situation is to conserve the rosin supply and to manuf. more if that is necessary. C. J. WEST

African woods for pulp. CLARENCE J. WEST. *Paper* 27, No. 24, 23, 34(1921).—There are several species of trees in Africa which attain pulp-wood size in from seven to ten years and which should give a strong long-fibered pulp. The quantity of bamboo on the West Coast of Africa is negligible. H. H. HARRISON

Ultramarine blue in paper making. LOUIS P. SCHWEITZER. *Paper* 27, No. 25; 12, 36(1921).—To det. the relative resistance of ultramarines to acids one g. of each sample to be tested is dissolved in 2 l. distd. water to which is added 150 g. saccharic acid. The sample whose discoloration proceeds the most slowly is most resistant. In practice to prevent possible decompn. from acid residues from the bleaching process it is well to add a little Na_2CO_3 to the soln. of the dye. The common adulterants to be found are plaster, potter's clay or sugar and glycerol. H. H. HARRISON

Utilization of bamboo for papermaking. *Bull. Imp. Inst.* 18, 403-27(1920).—A general article which discusses the general characters and distribution of bamboos, the occurrence and utilization in various countries, and the conversion of bamboo into paper pulp. C. J. WEST

Some puzzles in paper-making. F. HECCKFORD. *Paper-Maker Brit. Paper Trade J.* 61, 347-9(1921).—Ultramarine-colored papers may be discharged in a damp

warm atmosphere where the moisture dissolves the alum, permitting it to attack ultramarine with the evolution of H_2S . This in turn may combine with any copper from pumps or beater bars, in the paper to form little tree-like forms in the paper.

H. H. HARRISON.

The compound microscope and its value in the mill. I. L. GARTLAND. *Paper* 27, No. 25, 14-17, 36(1921).—The elements of the compound microscope, the prepn. of slides and the suitability of various filters in making photomicrographs of fibers are set forth.

H. H. HARRISON.

Filter paper—a reading list. CLARENCE J. WEST. *Paper Trade J.* 71, No. 15 (1920).—Contribution No. 16 of the Committee on Bibliography of T. A. P. P. I.

C. J. W.

Paper research literature. VI. A list of contributions of the staff of the Königl. Materialprüfungsamt zu Berlin. Compiled by WILLIAM HERZBERG. Translated and augmented by CLARENCE J. WEST. *Paper Trade J.* 71, No. 17 (Oct. 21, 1920); No. 18, (1920).—Contribution No. 17 of the Committee on Bibliography of T. A. P. P. I.

C. J. W.

Paper research literature. VII. A list of the contributions by members of the Bureau of Standards, Department of Commerce. Compiled by E. A. CURTIS. *Paper Trade J.* 71, No. 19(1920).—Contribution No. 18 of the Committee on Bibliography of T. A. P. P. I.

C. J. W.

The sizing of paper—a reading list. CLARENCE J. WEST. *Paper Trade J.* 71, No. 20(1920); No. 21, (1920).—Contribution No. 19 of the Committee on Bibliography of T. A. P. P. I.

C. J. W.

History of papermaking in the United States. MAUDE V. DICKINSON. *Paper Trade J.* 71, No. 21 (Nov. 18, 1920).—Contribution No. 20 of the Committee on Bibliography of the T. A. P. P. I.

C. J. W.

Blotting paper—a reading list. CLARENCE J. WEST. *Paper Trade J.* 71, No. 22(1920).—Contribution No. 21 of the Committee on Bibliography of T. A. P. P. I.

C. J. W.

The bleaching of paper pulp. CLARENCE J. WEST. *Paper Trade J.* 71, No. 24 (1920).—Contribution No. 22 of the Committee on Bibliography of T. A. P. P. I.

C. J. W.

Paper-making material. CLARENCE J. WEST. *Paper Trade J.* 71, Nos. 25, 26, 72; Nos. 1, 2, 3, 4, 5, 6, 7, 8, 9, 10 (Dec. 16, 1920—Mar. 3, 1921).—Contribution No. 23 of the Committee on Bibliography of T. A. P. P. I.

C. J. W.

The use of aluminium bronze in the paper industry. E. MESSMER. *Monit. papeterie* 52, 18, 65-6(1921).—Al bronze is valuable in paper mills, especially for bedplate bars and beater roll bars in the manuf. of fine and semi-fine papers. Reasons are given.

A. P.-C.

Use of casein for coating paper. R. MILLER. *Papeterie* 43, 157-8(1921).—Though casein gives fairly good results it is not as satisfactory as gelatin, as it is much more putrefiable and must be prepd. a relatively short time before use (less than 48 hrs. in summer). The addition of CH_3O to make it keep has the disadvantage of thickening the soln. and prevents it from working properly. M. has found by long experience that borax or NH_3 (10% of either) is the most satisfactory solvent, and prefers borax to NH_3 . But when the casein is to be mixed with substances having an acid reaction, it is well to add a slight excess of NH_3 to prevent the casein from thickening. Foaming in the sizing tub can very readily be prevented by the addition of a little milk or spirits of turpentine to the coating soln., or by allowing $AmOAc$ to drop slowly on the surface of the soln.

A. P.-C.

A new method of sizing. *Paper* 27, No. 18, 13(1921).—The principal feature of the "Zellkoll-Amal" process of sizing fine papers is that animal glue is added to the

pulp in the engine not in soln. but as a jelly made by the addition of formaldehyde or formate of alum to the glue soln. As the glue is added in a semi-solid state it reaches the pulp almost completely and a much greater part of the loading remains in the paper than in paper sized otherwise. These papers do not dust in the printing press, and the writing pen does not tear small particles from them. Using formate of alum in combination with animal glue, BaSO_4 may be used as loading, producing remarkably strong, hard papers for book, bank, writing, drawing, document and blue-print papers.

H. H. HARRISON

Rosin and rosin sizing. E. SUTERMEISTER. *Paper* 27, No. 13, 22-3(1920).—The sizing value of rosins increases in passing from the darker to the lighter grades, though the difference in favor of the lighter grades is hardly great enough to justify any marked difference in price. The sepn. of rosin which takes place when size emulsion stands three or four days does not seem to have any harmful effect on its sizing.

H. H. HARRISON

Notes on bleach and bleaching. FRANK D. LIBBY. *Paper* 27, No. 25, 18-9, 36(1921).—An outline is given of present practice in bleaching. Rag stock is considered as an example of an easily bleaching stock and sulfite as a hard bleaching stock. Hot and cold processes, the use of acid and antichlors, ordinary washer methods and the use of special equipment are discussed.

H. H. HARRISON

Sulfite carbon. A. KLEIN. *Papier-Ztg.* 46, 634-5(1921).—A description is given of an app. by the use of which 1 ton of sulfite liquor gives 350 kg. carbon with about 7000 cal., 3.5 kg. MeOH and, by fermentation, 36 kg. EtOH, at an expense of 140 kw.-hours elec. energy and 1000 kg. steam.

C. J. WEST

Fermentation of cellulose (FOWLER) 16.

CLARK, J. J.: *The Manufacture of Pulp and Paper*. Vol. I. Arithmetic, Elementary Applied Mathematics, How to Read Drawings, Elements of Physics. New York: McGraw-Hill Book Co. 441 pp. \$5.

24—EXPLOSIVES AND EXPLOSIONS

CHARLES E. MUNROE

Some properties of explosives. ROBERT ROBERTSON. *J. Chem. Soc.* 119, 1-29 (1921).—The lecture is divided into 2 parts, (I) dealing with the influence of constitution and physical condition and treating on (1) heat of formation; (2) heat of explosion and gases evolved; (3) chem. stability; (4) sensitiveness to shock; (5) rate of detonation and (6) pressure developed, and (II) dealing with the *explosive properties of the amonals* and covering for them specifically, the items detailed under (I) for explosives in general. Quant. detns. have been made for each item and the results are presented and discussed. The heats of combustion, from which the heats of formation are deduced, are being published by Garner and Abernethy. The sensitiveness to shock was detd. by Rotter's falling-weight instrument, in which the result of the blow is evaluated by a quant. measurement of the gas produced at the different heights of fall when the blow delivered has sufficient energy to cause decompn. of the explosive and gas to be evolved. The sensitiveness is expressed in ratios, known as "*figures of insensitiveness*" which express, in terms of a standard explosive, the relative energies of the blows required to produce explosions of equal degrees of completeness throughout the scale from incipient to complete detonation. The pressure developed was detd. by Hopkinson's app. (C. A. 9, 151), sometimes known as the "*pressure bar*." This app. was found especially valuable in investigations of the designs of such mechanisms as detonators, fuses and gages.

The amatols were the pourable mixt. of 40 pts. NH_4NO_3 and 60 pts. TNT and the dry mixt. of 80/20 designed to meet the war demand that could not be met by TNT alone. These amatols ultimately became the only filling for land service shell, aerial bombs and other munitions and the manuf. eventually reached an output of 4000 tons a week. Extreme care must be taken that the NH_4NO_3 is free from $\text{C}_4\text{H}_5\text{N}$ or NH_4SCN .

CHARLES E. MUNROE

Recent development of explosives. HAJIME KISHIMOTO. *J. Chem. Ind. (Japan)* 23, 724-92(1920).—Factors for detn. of brisance of the various explosives are given. The past history of and present tendency of the development of explosives in the world are considered in detail. The future of the industry depends on close coöperation with the dye industry, and supply of raw materials by distn. of coal, cracking of petroleum, manuf. of fuming H_2SO_4 and nitrogen fixation.

S. T.

Notes on the reactions of fulminate of mercury with sodium thiosulfate. F. H. AND P. V. DUPRÉ. *Analyst* 46, 42-9(1921).—Because of the high cost of KI a substitute for use in the titration of $\text{Hg}(\text{ONC})_2$ by $\text{Na}_2\text{S}_2\text{O}_4$ was found in HBO_3 , which proved even more efficient than KI both at ordinary and elevated temps., since it considerably increased the rate of rise in temp.; because soln. of large crystals of $\text{Hg}(\text{ONC})_2$ take time, this characteristic of HBO_3 is especially useful. Sufficient HBO_3 must be used to form $\text{Na}_2\text{B}_4\text{O}_7$. Tests of destruction of waste fulminate by $\text{Na}_2\text{S}_2\text{O}_4$ showed that the $\text{Hg}(\text{ONC})_2$ tends rapidly to settle and that to obtain promptly the complete conversion of the fulminate (1) efficient agitation must be continued throughout the operation and (2) a quantity of $\text{Na}_2\text{S}_2\text{O}_4$ equal to 3 times the wt. of the $\text{Hg}(\text{ONC})_2$ in the form of a 20% soln. must be used. A serious source of danger in using less $\text{Na}_2\text{S}_2\text{O}_4$ lies in the fact that the NaCN soln. formed may dissolve and hold unconverted $\text{Hg}(\text{ONC})_2$. Heaven (C. A. 12, 2440) having questioned the accuracy of Marshall's equation, a study was made of the products of the reaction of 2 equivs. of $\text{Na}_2\text{S}_2\text{O}_4$ and 1 of $\text{Hg}(\text{ONC})_2$ in soln. after short boiling leading to $\text{Hg}(\text{ONC})_2 + 2\text{Na}_2\text{S}_2\text{O}_4 + 2\text{H}_2\text{O} \rightarrow \text{HgS} + 2\text{Na}_2\text{SO}_4 + \text{NH}_4\text{CNS} + \text{CO}_2$. The exptl. data of each investigation are presented in graphs.

CHARLES E. MUNROE

Possible uses of corncob cellulose in the explosives industry. L. G. MARSH. *J. Ind. Eng. Chem.* 13, 296-8(1921).—It appears that the only use for corncob cellulose in the explosives industry at the present time is as a carbonaceous absorbent for liquid ingredients, such as nitroglycerin, in the manuf. of dynamite. For that use it must compete with such materials as wood pulp, sawdust, cornmeal, charcoal, peanut hulls, rice hulls, and similar materials, all of which have properties advantageous for special grades of dynamite.

CHARLES E. MUNROE

Viscosity of nitrocellulose. EDWARD C. WORDEN AND LEO RUTSTEIN. *Kunststoffe* 11, 25-28(1921).—Review of the literature.

C. J. WEST

Initiation of military explosives. WILLIAM A. CORLEY. U. S. Navy. *J. Franklin Inst.* 191, 87-120(1921).—Sections are devoted to an historical review of the subject, ignition and the ignition system, detonation, the detonating system, initiating compositions, and a bibliography. "Little can be said about the future of the org. detonating agents; those proposed so far appear to be too sensitive to shock and too liable to deterioration of one sort or another to be of any practical value for military use. The mere fact that there are org. substances which are more effective detonating agents, wt. for wt., than any of the metal compds. is nevertheless important, in that it shows that there is a possibility of finding somewhere among the org. compds., with their wide range of properties, a detonating agent more useful than any we now know."

JOSEPH S. HEPBURN

French chemical industry during the war. A. HALLER. *Bull. soc. encour. ind. nat.* 119, 761-825(1920); *Nature* 106, 831-4.—An account is given of the way in which

the requirements of the fighting forces of France for munitions were met. The peak for production in France appears to have been reached in July 1917. The war productions, in metric tons per day, were before 1914 and in July 1917 for poudres B 15 and 370, for nitro explosives 6 and 700 and for chlorate explosives 4 and 176, resp. Before the war phenol for picric acid came from Germany, likewise many other of the materials used in manuf. were imported. Hence processes for their manuf. had to be developed and factories erected in France after war began. Factories under fire, such as the oleum plant at Thann, were taken down and away at night for erection elsewhere. Before the war 87 plants produced 13,500,000 tons of 53° Bé. H_2SO_4 but this output was reduced 15–20% by enemy occupation, yet by Jan. 1917 there was being produced 80,000 tons of 66° Bé. and 20,000 tons of 20% oleum. Of the latter 1.5–1.9 tons were used per ton of nitrocellulose produced, and 2.2 tons per ton of TNT. Before the war synthetic HNO_3 was made in France by the Pauling arc process at the rate of 2 tons of 50% acid per day. A Birkeland and Eyde plant erected after the war began reached a monthly output of 300 tons HNO_3 . In 1917, following the sinking of cargoes of niter by submarines, carbide plants were developed for an output, through NH_3 oxidation, of 500 tons HNO_3 and 150 tons NH_4NO_3 per day. NH_4NO_3 , largely used in *schneiderite*, (NH_4NO_3 88, dinitronaphthalene 12 parts), and other explosives, was made also by the straight neutralization process, by metathesis of Norwegian $\text{Ca}(\text{NO}_3)_2$ and $(\text{NH}_4)_2\text{SO}_4$, or of NaNO_3 and $(\text{NH}_4)_2\text{SO}_4$, the latter process being worked out by Fosse and Danne. The enormous requirements for alc. were met by distn. of beets, molasses, and cider; saccharated grain, horse chestnuts or sawdust, and from confiscated absinthe and liqueurs. The Dept. du Nord, where 2,000,000 hl. of alcohol per year and 6000 hl. of brandy per day had been produced, was occupied by the Germans. France had, before the war, depended for large supplies of hydrocarbons on foreign sources, among them, Germany. The need was met largely by Borneo petroleum, gas strippings and erection of by-product coke ovens. Gun cotton reached an output of 433 tons daily. Following the explosion on the battleship "Liberté" in 1911, large quantities of gun cotton were thrown into the sea outside Toulon. This was recovered in excellent condition and utilized. Liquid N_2O_4 was produced at the rate of 95–110 tons per day. It was used in making *anilite*, for airplane bombs, by admixt. with a hydrocarbon. Paraffined NH_4ClO_4 was found too sensitive to shock for use as a bursting charge for 75-mm. shells but it was extensively used for trench-mortar bombs, hand grenades and airplane bombs. NaClO_4 and a mixt. of NH_4ClO_4 , 61.5 NaNO_3 , 30 and paraffin 8.5 parts were also used. There were produced electrolytically 79 tons NH_4ClO_4 and 77 tons NaClO_4 daily. The manuf. of nitrocellulose and many of the nitro compds. is described. The method of making picric acid from C_6H_6 by use of an Hg catalyst is condemned because of poor yields and the likelihood of the picric acid becoming sensitive from the presence of small amts. of Hg picrate.

CHARLES E. MUNROE

Dust explosions. DAVID J. PRICE. *Chem. Met. Eng.* 24, 473–5(1921).—Deals with methods of prevention such as "grounding" for protection against static elec. charges, avoidance of "choke-ups" which permit ignition through friction, devices for preventing breaks of elec. lamps and circuits, and introduction of inert dusts or gases to prevent propagation of explosions. An explosion cannot occur with starch dust in an atmosphere containing less than 12% of O and for grain elevator dust probably less than 14–14.5%. Flue gas seems indicated for use. Explosions during dust removal suggest that the exhaust fan be located beyond the dust collector. A variety of problems in the chemistry and engineering features of this field are presented (cf. C. A. 15, 946).

CHARLES E. MUNROE

Note on the rate of reaction of picric acid with nitrating acid. D. L. HAMMICK. *J. Soc. Chem. Ind.* 40, 26T(1921).—Tests by heating picric acid with a nitrating acid

showed that even at comparatively high temps. the rate of destruction of picric acid by them is too slow to affect the yields obtained in the nitration of C_6H_5OH .

CHARLES E. MUNROE

Explosion from sugar dust. ANON. *Z. Ver. deut. Ing.* 65, 13(1921).—As a result of serious explosions during 1916–17 in sugar factories tests were conducted in the gas and dust testing gallery at Neukirchen. The ignition point of fine dry sugar dust was fixed at 425° and it was shown that the capacity for explosion from various sources of ignition varied with the concn. of sugar dust in the air, being for an are light 72 g. sugar per cubic meter of air, elec. sparks 370 g. and flame of petroleum lamp 180 g. Sugar-air mixts. can be ignited by wrought Fe at a dark red heat and hence by hot boxes. Low concns. become explosive by slight addition of CH_4 . Safety precautions are given.

D. J. PRICE

Analyses of air from burning buildings. S. H. KATZ. Bur. of Mines, *Repts. of Investigations* No. 2185(1920).—Vacuum bottles for taking samples were sent to fire chiefs in 25 cities. At the time this rept. was prepared hut 11 samples had been received. The results of the analyses of these, together with pertinent data, are presented in a table from which it appears that 8 contained no CO, one taken above ground contained 0.03% and 2 taken below ground 0.1 and 0.35% of CO, resp. None was deficient in O. The hazard from CO is much greater below ground because of poor ventilation. The highest amt. of CO was found in a cellar where fire was burning among piled cases.

CHARLES E. MUNROE

The nature of flame movement in a closed cylinder (WOODBURY, *et al.*) 21.

Matches. S. HATAKEYAMA and C. FUNAI. Japan 36,227, Apr. 21, 1920. A mixt. of 7 g. Cu_2C_2 , 12 g. $KClO_3$, 0.7 g. S, glue and H_2O is applied to the stick and 1 g. red P, 1 g. Sb_2S_3 , glue and H_2O to the box. The Cu_2C_2 is prepd. by passing C_2H_2 into an ammoniacal soln. of Ca_2Cl_4 .

25—DYES AND TEXTILE CHEMISTRY

L. A. OLNEY

Dyeing and its connection with the rubber industry. HENRY J. THOMPSON. *Am. Dyestuff Reporter* 7, No. 19, II, 20–1(1920).—The rapid expansion of the rubber industry, and consequent demand for more colored effects, has raised many new problems for the dyer. Since rubber fabrics are made without reference to their dyeing qualities, the dyer must know the processes through which the fabric has been put in order to select colors for successful dyeing. These processes and the appropriate classes of dyes for various rubber fabrics are discussed.

L. W. RIGGS

Fastness to washing. L. PELLET JOLIVET. Abstracted by Benedict C. Heyman. *Am. Dyestuff Reporter* 7, No. 23, Sec. 2, 26–7(1920).—A hank of wool of 20 g. weighed dry was placed in each of several large flasks containing concd. H_2SO_4 , concd. HCl and a 0.02 N soln. of NaOH and allowed to remain 5 days. The liquid was then decanted and measured. The wool retained 4.9 g. out of 24.5 H_2SO_4 , 3.3 g. out of 18.25 HCl, and more than half of the NaOH. To the treated wool H_2O was added in 500-cc. portions until the acid or alkali was practically washed out. This required 15 washings for the acids. Nearly all of the NaOH was taken out in 2 washings. Wool samples treated with H_2SO_4 or HCl of varying concns. also with H_2O or NaOH showed wide variations in their absorption of methylene blue and of Ponceau 6R; NaOH favoring the absorption of the blue and H_2SO_4 that of Ponceau 6R. These dyed samples were dipped into a beaker containing 200 cc. H_2O and the amt. of dye washed off was greatest from the sample

treated with NaOH and least from H_2SO_4 or both colors. The dyed samples were then worked in a Soxhlet until the color was stripped. Here the greater resistance to stripping was with the samples from the H_2SO_4 bath. The water extd. a greater wt. of solids than the wt. of the dyestuff absorbed, showing that more than dyestuff was taken from the wool.

L. W. RIGGS

Notes on manufacture of rhodamines. I. RAFFAELLE SANSONE. *Color Trade J.* 8, 84-8(1921).—The importance of these dyes and the present demand for them are discussed, and a brief résumé is given of the general method of prepn. involved. Notes on the prepn. of some of the intermediates used, and details of the prepn. and working up of the basic phthalein, are added. Diagrams of app. used are given.

F. S. BRATTIN

Laboratory experiments in rendering dyes on textiles fast to sunlight. FREDERIC DANNERTH and KURT GEBHARD. *Am. Dyestuff Reporter* 8, No. 1, Sec. 2, 20-2, No. 6, Sec. 2, 13-7(1921).—"The photo-chemic action of light on dyes results in auto-oxidation, and the O attaches itself to the dye in the peroxide form. In the presence of moisture the \cdot -hydroxyl and \cdot -perhydroxyl ions play an important part in the formation of the labile dye-peroxide-hydrates." "Light fastness is not an unchangeable property of a particular dye but is dependent in a rather high degree on the 'dye carrier.'" A method was sought for preventing a subsequent reaction between the dye and O, or for changing the usual course of this reaction on the basis of the following thesis: "If a dye-peroxide possesses the character of a dyestuff, and the shade of the former is not materially different from the shade of the latter, it must be possible to prevent the reaction between the dye and O by introducing such substances into the system which have the power to unite with such atomic groups in the dye mol. as have a tendency toward the formation of a 'peroxide.'" This may be accomplished (1) by treating the dye itself so that the groups which react in the presence of light are rendered inactive. Helindron Yellow 3GM and sulfur dyes respond to such treatment. (2) By after-treatment of colored fibers. The fact that the peroxide is at first only loosely and further the way in which it is attached to the coloring part (by partial valence) indicate that it is necessary to use for the satn. of the open or 'ionized' valence such compds. as are capable of forming additional products by means of partial valence. "These methods are discussed at length. After-treatment with glycocoll and either $Al_2(SO_4)_3$, $ZnCl_2$, or $CrCl_3$ increased the fastness of Dianil Pure Blue PH and of malachite green; glycocoll and $CuSO_4$ had almost no effect. Brilliant Benzo Violet B was increased by glycocoll with $ZnCl_2$ but not with the other metallic salts. "Glycocoll apparently reacts with active nuclear hydrogen atoms." In many cases oxyacids in the absence of metallic salts act as a "bridge" or else they protect the active H atoms. Urea and thiourea act by forming addition products. Sodium molybdate, phosphotungstate, phosphite and metaphosphate form stable addition products and complex compds. They are useful with a few dyes. Metaphosphoric acid and its salts have a wide application. $NaNO_2$ and $Na_2S_2O_3$ are used in a few cases, the latter is applicable to silk. Dye-fiber can be rendered inactive by means of a second dye in a few cases such as the combination of flavanthrene with indanthrene.

L. W. RIGGS

Dyeing of mixed goods of wool and cotton. GILES LOW. *Am. Dyestuff Reporter* 7, No. 19, Sec. 2, 22(1921).—The relative percentages of wool and cotton fibers are detd. by dissolving the wool from a weighed sample with dil. NaOH. Directions are given for making preliminary lab. tests upon a sample of the batch to be dyed. Among the colors which dye cotton and wool practically the same shade are benzo-purpurins, Congo Reds, Garnets, Pink 2B, Orange R, Chrysamine, Chrysophenine, the direct greens, Fast Blue RW, Brown GXR, and the majority of direct blacks. Among colors which dye cotton deeper than wool are Fast Red F, the Stibbene Yellows,

Fast Yellow NN, all the sky Blues; Blue 2B and 3B, Violet N and R. An alk. bath retards the dyeing of wool and frequently accelerates the dyeing of cotton, while an acid bath acts in a directly opposite manner. When necessary an alk. bath should be made acid with HCOOH or AcOH , or an acid bath should be made alk. with Na_2PO_4 or borax. Wool will continue to dye from very dil. baths but cotton requires more concn. Below the boil color feeds on to the cotton; at the boil wool is favored. By properly managing these conditions equalization of shade may be effected. Sometimes the two-bath process must be used. This consists in dyeing the wool first in an acidified bath, then bringing the cotton up to shade in a bath below the boil. These preliminary tests should be tried on a sample cut to a wt. representative of the batch to be dyed, and the miniature bath should correspond to that used in the dyehouse. Cloth to be dyed should be carefully inspected to be certain that the cotton is properly scoured.

L. W. RIGGS

Khaki on cotton cloth. WILLIAM H. CADY. *Am. Dyestuff Reporter* 7, No. 23, Sec. 2, 11-15(1920).—C. gives an historical account of the development of the khaki shade for the protective coloring of armies. S dyes are mainly used for dyeing khaki in America and the process is conducted as follows: The necessary dyes and chemicals are dissolved in boiling water in the steerage tanks, a typical formula for 500 gal. being, S yellow-brown 80 lbs., S olive 80, S yellow 20, calcined Na_2S 140, Na_2CO_3 24, sulfonated castor oil 100. This liquid is piped directly into the padding box through which the cloth is drawn at the rate of 60 to 70 yards per min. It is best to pass the fabric through the bath twice, squeezing after each passage with a 3-roll mangle. On leaving the bath the cloth travels 20 to 30 ft. in the air in order partly to oxidize the color and is then thoroughly washed before chroming. The chrome liquor is made by dissolving 5 lbs. each of $\text{Na}_2\text{Cr}_2\text{O}_7$ and CuSO_4 in 100 gal. boiling water in a storage tank, and adding enough AcOH to keep the bath constantly acid. The liquid is fed continuously into the chroming box. The temp. of the bath should be 45 to 50°; a higher temp. has a tendency to strip the color. Dyeing mineral khaki as practiced in England and America is described, also direct, wood, and vat khaki. To det. the process used with a sample of cloth proceed as follows: (1) Boil in byposulfite and NaOH soln., direct khaki is permanently decolorized or reduced to a pale yellow; other khakis are only temporarily affected. (2) Boil in 5% HCl , mineral khaki is entirely destroyed, wood khaki turns red-brown and the acid liquid yellowish. S and vat khaki are not affected. On neutralizing the acid with NaOH , wood khaki becomes darker. (3) S khaki mixed with H_2O , HCl and Sn crystals in a test-tube and boiled a few sec. yields H_2S , shown by blackening $\text{Ph}(\text{C}_2\text{H}_5\text{O}_2)_2$ paper held over the mouth of the tube. (4) Ignite and exam. ash. Fe and Cr in large amts. indicate mineral khaki. Cr with little or no Fe points to S or wood khaki. Absence of metals suggests vat or direct colors; infrequently S colors. There is no special test for vat dyes, the most helpful one is the change of color when reduced with byposulfite, the original shade returning on subsequent oxidation.

L. W. RIGGS

Spray printing. BRUNO WALTHER. *Deut. Färber-Ztg.* 57, 105-6(1921).—The essential app. for spray printing consists of an adequate work table, a spraying outfit selected according to the work to be done, an exhaustor for the removal of dye spray, and means of furnishing steam pressure. The spraying liquid must not be viscous or contain any sediment. Recipes for compounding alc.-sol., basic, acid, and substantive dye liquids are discussed in detail. Basic dyes are recommended for cotton, acid dyes for wool and silk.

L. W. RIGGS

Pelt and fur dyeing. W. FUCHS. *Deut. Färber-Ztg.* 57, 145-6(1921).—All pelts are placed in a 6° Bé. bath of H_2SO_4 and chromic oxide for 10 to 12 hrs. at about 20°. The pelts are then removed, drained, rinsed, and usually washed with soap. After rinsing all of the alkali the fat is removed by manipulating the pelts for about 5 min. in a 2% chloride of lime soln., without soda, rinsed in cold water and placed in a

lukewarm HCl bath for 15 min. The pelts are then removed, well rinsed and are ready to be dyed. The treatment above described increases the affinity of the pelt for the dyestuff. Recipes for mordants and dye baths are given for black, gray, and 4 shades of brown with details for their use. A soft feel to the hair is produced by passing the pelts through a bath containing 10 g. Marseilles soap, 2 olive oil, and 0.5 NH₃ in 1 liter of water, after which the pelts are rinsed, centrifuged and dried. L. W. RIGGS

Comparative studies of the chemical constitution of tussah silk. RYUGO INOUE, SUZUKO IWAOKA AND MASARU HIRASAWA. *J. Tokyo Chem. Soc.* 41, 876-98(1920); cf. *C. A.* 4, 223, 596, 1052.—Comparative studies of silk cocoons of Japan (*Ariake*), and of Manchuria were made. Since these two kinds of cocoon have entirely different physical properties, and the foods and climates are so dissimilar, the object of the work was to compare the chem. compn. of silks. The results of the analysis are: 100 g. of dry cocoon from Manchuria contains 10.871 g. H₂O, 89.129 g. solid. Of the total solid, 1.231% is ash, 18.44% N. On hydrolysis 100 g. dry material gave, in g., glycine 16.796, alanine 11.865, leucine 0.248, aspartic acid 4.084, glutamic acid present, serine 0.472, phenylalanine 1.184, oxyproline 0.181, proline 0.233, and tyrosine 3.858. 100 g. of the Japanese (*Ariake*) cocoon contains 10.33 g. H₂O, 89.68 g. solid; 100 g. of solid contains 2.004 g. ash, 18.24 g. total N. On hydrolysis, 100 g. of the dry cocoons gave (in grams), glycine 12.38, alanine 15.27, leucine 0.27, aspartic acid 2.37; glutamic acid present, proline 0.26, phenylalanine 0.37, serine 0.55, tyrosine 6.62. In view of uncertainty of the ester method used for isolation of amino acids, these two varieties of the tussah silk are considered to be chem. identical, and differences in physical properties of cocoons must be due to other factors than the difference in silk. These results were compared to chem. compns. of tussah silk of Japanese (cf. *C. A.* 4, 1052), of Hindoo (cf. *C. A.* 4, 596), and of Chinese (cf. *C. A.* 4, 223) origin, and found to be quite analogous, *i. e.*, glycine, alanine, tyrosine are most abundant, and then aspartic acid, the remaining amino acids being present in very small quantities. It is similar in compn. to ordinary silk, in that the first 3 amino acids are dominant, but differs in respect to the ratio of alanine to glycine. In silk the glycine content is more than 20%, being always more than alanine, but in tussah silk it is the reverse. The amt. of the fraction insol. in hot HCl at the time of hydrolysis, is also much larger in tussah than in domestic silk; other wild silk has the same characteristics. S. T.

Raw silk classification. L. C. LEWIS. *Am. Dyestuff Reporter* 7, No. 19, Sec. 2, 18-9 (1920).—Faults in the finished product may be charged to dyeing operations when they are actually caused by differences in the quality of the raw silk. Tests must be made at 21° and 65% relative humidity. The values detd. are evenness, cleanness and cohesion. These physical tests are described in detail, the results on a com. sample are reduced to figures, classified and arranged in a chart. L. W. RIGGS

Recent applications of solvent scouring—treatment of delicate piece-goods. HARRY HEY. *Text. Mercury* 64, 232(1921).—In degreasing, goods may be packed tightly but under such a condition very little of the dirt is removed. By packing loosely the wool does not act as a filter and much dirt is removed. In the solvent scouring process the materials when exposed to air are coated with a condensation product which is partly water. By using soap at this point the grease dissolved in the solvent and the water present are emulsified thus carrying away the dirt. Solvents at present used have a much higher h. p. than those in use before the war, which makes them more difficult to recover and more expensive. Research is now being conducted on the problems of solvent scouring. L. W. RIGGS

Manufacture of textile soaps and oil preparations for special work. OSKAR GAUMNITZ. *Deut. Färber-Ztg.* 57, 127-8(1921).—Detailed recipes are given for K oleate 50%, Na oleate 50%, finishing oil 25%, fulling oil, softening mixt., Turkey red oil, and lard oil. L. W. RIGGS

Estimation of toxic water-soluble dust (ISZARD) 1. Some industrial uses of gas [recovery of wool from cotton-wool mixtures] (BRODIN) 21.

Fiber of *Sesbania aegyptiaca*. T. MATSUOKA. Japan 35,952, Mar. 11, 1920. Stems of *Sesbania aegyptiaca*, Pers. are immersed in H_2O for a few days, cleaned, boiled with dil. $NaOH$, and bleached with $CaOCl_2$ soln. The product is used instead of hemp fiber.

Textile fiber from *Boehmeria tricuspidis*. C. OKASHIMA. Japan 36,075, Apr. 6, 1920. (Addition to 34,349). Bark of *Boehmeria tricuspidis*, Matsum. is heated with a soln. of $(NH_4)_2SO_4$ 2, $NaOH$ 0.5-1, $CuSO_4$ 0.1-0.3 and H_2O 1000 under 2-3 atm. pressure and bleached with a dil. soln. of $CaOCl_2$. The product has a silky luster.

Artificial silk. T. KOTANI and Y. YAMANO. Japan 36,063, Mar. 31, 1920. A viscous soln. is prepd. by mixing 3.75 kg. pulp, 1.88 kg. $NaOH$ of Bé. 30°, 188 g. drying oil, CS_2 , and H_2O . A paper string is treated with this mixt. and then successively with dil. $CuSO_4$ soln., dried in the air, passed through 10% mineral acid, washed with 1% Na_2S soln. at 70°, then with 1-2% HCl , washed and bleached with $NaOCl$ soln., washed with $NaHSO_4$ soln. (Bé. 2°), with dil. acid and dried at 30-50°.

26—PAINTS, VARNISHES AND RESINS

A. H. SABIN

New methods in the varnish industry. J. BUDOWSKI. *Farben-Ztg.* 26, 469 (1920).—The varnish industry has been built up on empirical methods largely because of the chem. complexity of raw materials and finished products. Recent investigations show that certain naphthenic acids prevent polymerization of tung oil, and some of their heavy metal salts add durability to varnishes. The results of these investigations are reported to have been successfully applied to large scale production.

F. A. WERTZ

o-Dichlorobenzene solvent as a constituent of fumigating paints. HENRY A. GARDNER. Paint. Mfrs. Assoc. U. S., *Circ.* No. 116, 7 pp. (Feb., 1921).— o - $Cl_2C_6H_4$ solvent, resulting as mother liquor from crystn. of p - $Cl_2C_6H_4$, can be considered as a liquid phase of a mixt. of *o*- and *p*-, in which the latter predominates. $D_{15.5}$ 1.27; flash pt., 121° F.; initial b. p., 140°; final b. p., 183°. It is miscible with practically all paint and varnish liquids, and the fumes from brushed pot paints thinned with it were found to kill roaches, etc., almost instantly, while similar paints thinned with turpentine or mineral spirits had no effect. Paints thinned with this solvent have greater penetration on wood; this suggests its use in priming coats for hard woods. Tests on its use in retarding fungous growths, and in paint and varnish removers, are being made. Its high sp. gr. and wetting power retard settling of pigments in paints contg. it. G. quotes Duckett (*C. A.* 9, 3114) to show that the vapor of o - $Cl_2C_6H_4$ is harmless to human beings, but is an excellent fumigant against roaches, clothes, moths, flies, mosquitoes, and similar insects. Illus.

F. A. WERTZ

Live and dead turpentines, the methods of their preparation and the products of their decomposition. E. I. LYUBARSKII. *Annales école mines Oural* 1, 61-112 (1919).—A lengthy review of the methods of extrn. of turpentine in different countries, its sept. into colophony and oil of turpentine and the chemistry of the components of the oil and of the compds. obtained by the destructive distn. of colophony. The material which exudes from incisions in the bark of live fir trees is called live turpentine, while that which is contained in the stems and roots of dead fir trees is called dead turpentine. Owing to its geographical position, Russia is not rich in live turpentine, while owing to the age-long practice of cutting down fir trees, it has an enormous reservoir

of dead turpentine. In a future article L. will give special methods for obtaining valuable product from this reservoir.

H. M. GORDIN

The composition and uses of Australian *Xanthorrhoea* resin. ANON. *Bull. Imp. Inst.* 18, 155-62(1920).—*X. hastilis* yields a yellow resin (yellow gum acaroid) of the compn.: moisture 3, ash 1.3, matter insol. in EtOH 13-14, matter insol. in Et₂O 23%, m. 97°. The red resin (red yacca gum) is obtained from *X. arborea* and *X. australis* and has the compn.: moisture 3.5, ash 0.24, matter insol. in EtOH 4, matter insol. in Et₂O 16%, m. 110°. A sample of red resin, purified by extrn. with EtOH, yielded 2% free and combined *p*-coumaric acid, 0.1% cinnamic acid, 0.1% stryacin, trace of aldehydes and a residue of a complex phenolic compd. Destructive distn. of the resin yielded 17% of an oily distillate of a phenolic nature. Oxidation by HNO₃ of the yellow resin yielded 30% of picric acid, while the red variety yielded about 25% acid. Possible application of the resins as substitutes for shellac and resin in varnishes and as dyestuffs did not give promising results.

R. L. SIBLEY

Automatic electric enameling oven. E. KRAMER. *Elec. J.* 18, 82-3(1921), 4 illus.—Detailed account of a modern installation.

C. G. F.

Coloration of zinc sulfide by the action of light and a method of manufacturing light-proof lithopone. YŪSHICHI NISHIZAWA. *J. Tokyo Chem. Soc.* 41, 1054-67 (1920).—Believing that coloration of ZnO might be due to presence of ZnS, N. mixed ZnS and glycerol on paper and exposed it to ultraviolet light. The glycerol showed a protective action against light. Monatomic alcs. do not have a protecting power, while polyatomic alcs. have. Of tartaric acid salts, Na, K, K H have weak or no effect while Zn, Ba, Ca and Rochelle salts protect as well as polyatomic alcs., the ZnS retaining its original color under several hrs. exposure to the light. A very minute amt. is sufficient. Similar expts. on paints show that the presence of linseed oil or turpentine does not destroy the protecting property of these org. compds. The different inorg. impurities were found to accelerate, more or less, coloration of the sulfide, but when the protector is added to these impurities, the sulfide maintains its original color. Of inorg. OH salts, only Mg and Ca compds. are as effective as glycerol. Coloration of ZnS by heat also could be prevented by these alcs. Expts. are cited which suggest that restoration of the color in the dark is due not to reoxidation of Zn, but rather to formation of complex salts. On these principles, a new process of making lithopone is devised (cf. Japanese Pat. 35345).

S. T.

Potash Prussian blue. E. F. MORRIS. *J. Oil Colour Chem. Assoc.* 3, 154-60 (1920).—A review. The drying of Prussian blue press cake is best carried out in a current of hot air since it gives a stronger and less "cindery" product than a vacuum drier. Concn. of acid, temp. of pptn., amt. of oxidant used, etc., vary the shade of the resultant blue. The most convenient method of analysis is to expose the blue to the vapor of NH₄-H₂O (sp. gr. 0.88) in a desiccator, allow excess of NH₄ absorbed to evaporate, and take up with H₂O. The insol. portion is largely a mixt. of Fe' and Fe'' oxides, and any traces of Cr present can be detected much more easily than if the blue has first been ignited. On lab. batches, mechanical stirring seems to produce blues of the same color as large-scale production, while hand stirring gives blues that are useless as guides for mfg. practice. M. suggests that the property of a Prussian blue mol. of varying its color without altering its staining power may be due to a variation in ions subject to the balancing electrical charges; and a study of these blues ought to give information on problems of colloid chemistry. Discussion of the paper emphasizes that if vacuum drying decreases tinting strength it must be accompanied by coagulation of pigment particles; and that variations in the tone of blues is not subject to strict chem. control.

F. A. WERTZ

Advantages of cadmium lithopone. PAUL S. WEBSTER. *Chem. Met. Eng.* 24, 372-3(1921).—Cd lithopone, in which the Zn of commercial lithopone is replaced by

Cd, shows good covering properties and a high tinting strength; 5% of it with 95% of standard lithopone gives a pleasing cream-yellow. This material might be made commercially from the soln. of Zn and CdSO₄ obtained in the process of their sepn. from the associated metals, and could probably be marketed at a cost of \$0.29 lb. (See C. A. 15, 634.)

F. A. WERTZ

Further development of the plastometer and its practical application to research and routine problems. HENRY GREEN. N. J. Zinc Co. *Proc. Am. Soc. Testing Materials* 20, II, 451-94(1920).—In the plastometer previously devised by Bingham and Green (C. A. 14, 1047), the container is modified so that the material under test on being forced through the capillary tube at known pressures, displaces air at a rate which is measured by a very sensitive gaseous flow meter. Detns. of plasticity of com. paint pastes show that their mobility varies widely while variations in yield values are not so great. Stiff, stringy pastes and all pastes contg. pigments capable of being ground in a small percentage of vehicle, have low mobility. Yield value depends on the wetting of the pigment and its particle size. Tabulated detns. on greases show their high plastic nature. A good paint will have a mobility of 0.2 to 0.5 and a yield value of 0.40 to 0.8. If a paint is otherwise good, the higher the mobility the better. The instrument gives mathematical definition to the character of plastics and is applicable to routine matching of the "body" of paints, etc., and to the study of oil absorption of pigments, degree of plasticity of clays, particle size, thinning of paints and pastes on aging, livering, stringiness of pastes, effect of colloids on the properties of paints, etc. The instrument modifications are described in detail, mathematical detn. of the yield value factor, and graphs and tables of results, presented. Bingham in his discussion of the paper shows that it is theoretically possible to measure plasticity by making only 2 measurements of flow through a single capillary. Mixts. with a very small pigment content appear to conform to the laws of viscous bodies rather than to those of plastics.

F. A. WERTZ

A new colorimeter for white pigments and some results obtained by its use. A. H. PFUND. *Proc. Am. Soc. Testing Materials* 20, II, 440-50(1920); cf. C. A. 14, 1251. —A detn. of the color characteristics of white paints by methods of mono- or trichromatic colorimetry have been unsuccessful because the departure from white is so slight that measurements are not possible; but the instrument developed accentuates the departures by multiple reflections. The theoretical degree of accentuation is calcd. by studying the change in brightness resulting from the introduction of 2 different grays into the colorimeter. This consists of a circular disk (A) whose surface is covered with the material under observation, and above which is another disk (B) whose lower surface is covered with the same material. A non-selective mirror and a photometer cube bring both the incident light and the multiple reflected light from A and B together in the field of an eye piece. By successively placing color screens of 460 $\mu\mu$ (blue), 550 $\mu\mu$ (green), and 625 $\mu\mu$ (red) in the eye piece and varying the intensity of incident light until photometric balances are established, numerical values for brightness of the above colors of known wave length are obtained, and these establish the color characteristics of the paint. Curves are given to show brightness in the above colors for various white paint pigments, changes in color of ZnO-linseed oil paints with age, etc. Detns. with this instrument in connection with detns. of hiding power with a cryptometer (C. A. 14, 637) show that the ratio of % increase in hiding power to % decrease in brightness is approx. 5 when the amt. of lampblack added to the paint is small, so that a slight sacrifice in brightness produces a large increase in hiding power. Addition of a trace of lampblack while reducing brightness of all colors, affects the red and green more than the blue, and the paint appears less yellowish and may be made almost non-selective. Measurements on a ZnO paint after addition of lampblack showed a decrease in bright-

ness of 3.5% and an increase in hiding of 17.5%; such a slight reduction in brightness still classifies the paint as a very bright white paint. Discussion follows.

F. A. WERTZ

Natural earth and chemically made pigments and their respective characteristics. E. W. STORRY. *Paint, Oil and Chem. Rev.* 71, No. 4, 10-1; No. 5, 10-1; No. 6, 10-1, 31-3(1921).—A review.

F. A. WERTZ

Tentative specifications for foots permissible in properly clarified pure raw linseed oil from North American Seed. Serial designation D51-18T. *Proc. Am. Soc. Testing Materials* 20, I, 678-9(1920).—Foots shall not exceed 2%. Cf. C. A. 13, 664; 14, 1049.

F. A. WERTZ

Tentative specifications for turpentine. Serial designation D13-20T. *Proc. Am. Soc. Testing Materials* 20, I, 680-89(1920).—The present standard specifications (A. S. T. M. Year Book 581-3(1918); cf. C. A. 10, 975), are revised by addition of methods for detection and sepn. of H_2O , for sampling from containers of various sizes, detailed directions for making tests and reagents, and table for correcting distn. points for variations in atm. pressure. Cf. C. A. 14, 1449.

F. A. WERTZ

Report of sub-committee III on testing paint vehicles. HENRY A. GARDNER, *et al.* *Proc. Am. Soc. Testing Materials* 20, I, 390-404(1920); cf. C. A. 14, 3804.—Revision of the heat test and omission of the I jelly test in the present specification are recommended. Reports of cooperating analysts on the detn. of hexabromide yields on linseed oil by the Steele-Washburn method (C. A. 14, 356) and the Bailey modification are tabulated.

F. A. WERTZ

The effect of heating linseed oil under pressure at constant temperature. SAMUEL COPPELY. *J. Soc. Chem. Ind.* 60, 19-20T(1921).—Pure linseed oil on heating at 250-60° in sealed glass tubes for varying lengths of time up to 42 hrs., becomes lighter in color, its sp. gr. increases almost linearly, viscosity increases slowly for the first 21 hrs. and then very rapidly until after 24 hrs. it is 50 times the original viscosity. The break in the viscosity curve at 21 hrs. coincides with the much less distinct breaks in the sp. gr. and acid no. curves, and suggests a fundamental change in the compn. of the oil. This is also indicated by the appearance in the oil after 21 hrs. of an Me_2CO -insol. portion which increases rapidly with further heating until after 42 hrs. most of the oil becomes insol. This product is probably identical with that observed by Morrell (C. A. 9, 1124). Sapon. values remained practically constant (cf. Krumhaar C. A. 11, 1314); I values decreased regularly, hexabromides by the Hehner-Mitchell method dropped from 43% to 0 in 7 hrs., showing that the unsatd. glycerides had polymerized into more satd. di-acid glycerides. The acid values rose to a constant value of about 2.4 times the original instead of continuing to rise indefinitely as when the oil is heated under atm. pressure and volatile products are allowed to escape. This may be due to an hydrolysis equilibrium between the moisture in the oil, and the glyceride; whereas heating without pressure permits volatilization of $C_2H_5(OH)_2$, or its decompn. into H_2O and acrolein, to cause further hydrolysis.

F. A. WERTZ

Varnishes, paints and pigments. R. S. MORRELL. *Third rept. on colloid chemistry, Brit. Assoc.*(1920).—A review treating drying oils, varnishes, paints and pigments from the standpoint of colloid chemistry.

JEROME ALEXANDER

Electrically heated enamelling ovens. WIRT S. SCOTT. *Elec. Rev.* 78, 499-502(1921).—A review.

C. G. F.

Airplane dopes. MAURICE DESCHENS. *Rev. prod. chim.* 24, 3-10(1921); cf. C. A. 15, 764.—General review of the history of the prepn. of airplane dopes, of their compn., of the methods of manuf. of the raw materials employed, of the various solvents and their properties, of the method of manuf. of the dopes, of their application to the planes, and of their properties when so applied. Some dope formulas (mostly cellulose acetate dopes), are given.

A. P.-C.

A new synthetic resin from benzylaniline. WALTER HERZOG. *Oester. Chem. Ztg.* 24, 16-17 (1921).—The patented production of resins by the action of FeCl_3 on benzyl halides (*C. A.* 9, 1849) and by condensation of secondary amines with HCHO , etc., in presence of HCl (Goldschmidt, *Chem. Ztg.*, 1905, p. 33), led H. to expt. on condensation of secondary amines in which a benzyl group forms one component. Benzylaniline was heated under a reflux condenser for 1 hr. with 10 g. HCHO (40%), 20 g. H_2O , and 1 cc. concd. HCl . The resultant resinous product is brittle, transparent, brownish yellow; it is probably a condensation of 2 moles benzylaniline with one of HCHO to form dibenzylidiaminodiphenylmethane and finally diphenyldiaminodibenzylmethane. It is easily sol. in 50 and 90% benzene, in trichloroethylene, and in warm turpentine. The reaction will also take place in an alc. medium but produces a redder resin. Organic acids and alkalis do not catalyze the reaction. The product differs from that obtained by Goldschmidt in that the reaction proceeds only to the formation of diphenylmethane deriva. and, therefore, produces a material much better adapted for the varnish industry.

F. A. WERTZ

The reclaiming and utilization of old films (DESCHEENS) 5. The constitution of abietic acids in rosin (GRÜN) 10.

Lake. A. LINZ. U. S. 1,369,252, Feb. 22. The Na salt of the color produced from diazotized *p*-aminophenetole and 2-naphthol-3,6-disulfonic acid is dissolved (190 lbs.) in 250 gals. H_2O at 80° and a soln. of BaCl_2 140 lbs. dissolved in 175 gals. H_2O at 80° is added with const. stirring. 100 lbs. of 70% blanc fixe pulp is then added, stirred, boiled, filtered, washed and dried or a lake in paste form may be obtained by omitting the drying. Other substances such as BaSO_4 , $\text{Al}(\text{OH})_3$, whiting or gypsum may be substituted for the BaCl_2 . The lake obtained possesses considerable brilliancy, is fast to light and is insol. in H_2O and in many org. compds. such as C_6H_6 , toluene, or linseed oil. It gives shades of a rich maroon mass tone with a bluish red undertone, and is suitable for use in inks or paints.

Lacquer for headlight reflectors. O. D. PLUMMER. U. S. 1,369,467, Feb. 22. Bright metal surfaces of headlight reflectors are coated with a soln. formed of 4.5 oz. of pyroxylin dissolved in a gal. of a solvent such as amyl acetate.

27—FATS, FATTY OILS AND SOAPS

H. SCHERUBEL

A new method for determining water in fats and oils. HANS ORTEL. *Chem. Ztg.* 45, 64 (1921).—The method for the detn. of H_2O in oils containing less than 3% by noting the rise in temp. when they are mixed with MgSO_4 and kieselguhr (*C. A.* 15, 768) is applicable where more H_2O is present if the sample be diluted with petroleum oil. Where the H_2O content of an oil is 3-15% use 4 g. of sample + 16 g. petroleum; with 15-30% H_2O use 2 g. of sample + 18 of petroleum; and with 30-60% H_2O use 1 g. of sample + 19 of petroleum. The rise in temp. must be corrected for the heat absorbed by the vessel in which the detn. is made and the sp. heat of the diluting oil. Having obtained the corrected max. temp. rise the % H_2O is found from the table of the previous article.

H. S. BAILEY

Importance of the refractive index for judging oils and fats. URZ. *Pharm. Monatshefte* 1, 162 (1920).—An address.

W. O. B.

Pure skunk fat. J. M. ANDERSEN AND E. C. MERRILL. *J. Am. Pharm. Assoc.* 10, 213 (1921).—A specimen of skunk fat was obtained from a recently killed animal and rendered at low temp. The fat was a pale yellow, oily liquid at 25° . At room

temp. under long standing a semi-solid fat sepd. At 13° the entire specimen coagulated. It had a peculiar odor and an acrid, bitter taste. The properties were: d_{40}^{20} 0.91107, sapon. no., 197.74, I no. 82.44, Hehner no., 95.28, acid no., 3.61, acetyl value, 10.98, n_D^{40} 1.4610. Unsapon. 0.25%; sol. acids, 0.544%. The properties of the mixed fatty acids were: m. 33° acid no., 202.01; I no., 79.62; n_D^{40} 1.4510. L. E. WARREN

Recovery and use of wool fat. G. HARTMANN. *Fisenach. Seifensieder Zig.* 48, 42(1921); cf. *C. A.* 15, 443.—The wash water from the neutral wool fat is mixed with milk of lime to carry down the fat. The resulting mud is filter-pressed, dried and extd. with a solvent; the lime-residue is used as a fertilizer; the wool fat soln. is treated with soda or potash to convert the Ca and Mg soaps into alkali soaps and these are washed out. The wool fat soln. is filtered through charcoal, the solvent removed by indirect steam and finished with direct steam at 110°. The final product conforms to the requirements of the German pharmacopeia. P. ESCHER

A fatty substance not used in Roumania. I. T. ULIC. *Bull. soc. chim. Roumania* 2, 77-8(1920).—A cheap fat for industrial purposes could be obtained from dolphins, which are abundant between May and Nov., near the coasts of the Black Sea. This fat contains, besides glycerides, cetyl palmitate and some valeric acid, $d = 0.935$. It has pharmaceutical uses (oleum delphini) and it could be used for soap and candles industries, and for tanneries. M. WEINBERG

The hydrogenation of oils. G. GROTE. *Chem.-Zig.* 45, 27-9(1921).—Largely a review of German patent processes and catalyzers for hardening oils. Three methods for making H are mentioned briefly and the importance of hard fats in the food, soap, and leather industries is discussed. H. S. BAILEY

The catalytic hydrogenation of cottonseed oil. LOUIS KAHLBERG and GEORGE J. RITTER. *J. Phys. Chem.* 25, 89-114(1921).—Following an historical review which develops the inadequate disclosures of patents which form the bulk of the literature, the authors give an exptl. review of a few known processes and then report a more extensive exptl. investigation from which they conclude: Ni is the best single metal catalyst; half Ni and half Co mixt. is more effective than either metal alone; ZnCO₃ freshly pptd. in the presence of suspended Al powder is a fair catalyst; Bi pptd. on charcoal and reduced with H at 350° is fairly active. Two new Ni catalysts were made: (1) Ni deposited on As-free granulated Zn in a satd. soln. of NiCl₂; this hardens the oil at atm. pressure at low temps. (2) NiCl₂ reduced with H at 180° to 250°; this works fairly well at 170°. JEROME ALEXANDER

Castor oil industry and uses of the oil. A. BERGER. *Rev. gén. sci.* 32, 74-8 (1921).—Discussion of the culture, extrn., refining and uses of this oil. E. S.

Refining practice and theory. R. H. FASH. *Cotton Oil Press* 4, No. 11, 45-8 (1921).—Chemically the refining of vegetable oils is a problem in colloids. It has been noticed that oils from mills where steam was blown into the meats during cooking refined with less loss and a firmer soap stock than where cold water was used. This is probably due to a coagulation of the albumins which, if not coagulated, act as protective colloids during the refining. If during the refining with NaOH solns. the oil and lye be intimately mixed the loss is less and the color better than where less surface action is produced, due to poor agitation. With high-acid oils a "break" occurs quickly and as the agglomerated particles enclose free oil and unused NaOH a larger excess of lye is needed than with oils low in free fatty acids. If the protective colloids (albumin, etc.), could first be removed from the oil the free fatty acids could then be neutralized with weaker lyes with a saving in refining loss. H. S. BAILEY

Proposed method for the analysis of cottonseed. F. N. SMALLEY. *Cotton Oil Press* 4, No. 11, 44-5(1921).—The method proposed has been used successfully. It is

much quicker than the old official method of the Am. Oil Chem. Soc. *Method*.—Shake the sample as received on a 6-mesh sieve to remove dirt. Pick out trash, and mix well the sample thus cleaned. *Moisture*.—Weigh 5 g. of whole seed into moisture dish and dry for 5 hrs. at 100°. Calc. loss in wt. as moisture. *Oil*.—Weigh 5 g. of whole seed into a canvas bag (No. 10 canvas), and dry at 100–105° for 2 hrs. After this partial drying, which is designed to make the sample brittle, pound it in the bag. Place the bag and all in a filter paper and ext. for 2 hrs. Remove from the ext. app. and paper, allow the gasoline on the bag to evap., repound and re-extract as before for 3 hrs. Evap. the gasoline from the ext. and weigh the residue. Report as oil in seed. This method gives from 0.25 to 1.0% higher results than the old procedure, owing to the fact that the seeds have been dried and in the given extn. period therefore ext. faster. The method is more accurate than the old one, being independent of H₂O detn. and is cheaper, as the time formerly required to pick and cut the seed is eliminated. H. S. BAILEY

Some observations on the heating of cottonseed. JOHN MALOWAN. *Cotton Oil Press* 4, No. 11, 47–9 (1921).—To study the effect of pressure, moisture and ventilation on the spontaneous heating of stored cotton seed, prime seed were moistened and placed in insulated wood bins 3' × 3' × 5'. Some of these were ventilated by natural draft through perforated pipes in the bottom and holes in the cover and others tight. Weights of 200 lbs. per sq. ft. were put on ventilated and tight bins, and some were unweighted. The results show that neither pressure nor ventilation affects the rate of heating, but where the seeds are compressed so air cannot pass through them the rate of cooling off after heating is greatly retarded. Artificial ventilation will not prevent heating except as it dries the seed, but is of great assistance in cooling hot seed. Seed whose germinating processes have been killed will still heat and both oxidation and fermentation take place. Since it was found that during the heating O is used up and CO₂ evolved, further expts. were conducted in Erlenmeyer flasks, the quantity of CO₂ instead of the temp. being measured. Details are given of numerous expts. made in flasks, to study the effect of treating seed with disinfectants, holding at different temps. and in H and O atms. Almost no CO₂ was evolved in the flasks containing H₂ and none of the usual disinfectants except NaCl and those containing or producing acid appreciably retarded the liberation of CO₂. H. S. BAILEY

Further notes on sampling copra. P. W. TOMPKINS. *Cotton Oil Press* 4, No. 11, 46 (Mar. 1921); cf. C. A. 14, 3327.—Rule 204 of the Foreign Commerce Assoc. requires that in sampling copra pieces must be taken from at least every tenth sling load. This is none too often as it means only about 600 lbs. to a shipload of 1050 tons or 540 lbs. in loading 30 box cars. This large sample should be quartered down to 100–200 lbs., a portion retained for "type" samples and the remainder cut, quartered and as the size of the particles is reduced the sample made smaller until suitable for the lab. H. S. BAILEY

Colloid chemistry of soap. I. J. W. MCBAIN. *Third Rept. on Colloid Chemistry, Brit. Assoc.* 1920.—Includes constitution in alc., hydrolysis, hydrolysis-alkalinity and products of hydrolysis; ionic micelle and their properties; physical properties of soap solns.; solidification and gelatinization of soap solns.; effects of additions; detergent action. JEROME ALEXANDER

Improved centrifugal separation of oil from soap stock. ARTHUR DELAFONTAINE. *Chem. Age* (N. Y.) 29, 64 (1921).—By refining oil first with caustic, using just enough to neutralize the fatty acids, and adding enough Na₂CO₃ to form a firm soap, a clean sepn. can be made by a centrifuge. D. has designed a centrifuge which does this satisfactorily. The oil is fed to the lowest part of the machine and a baffle at the bottom is so arranged as to prevent the oil from traveling in a direct trajectory to the outlet of the centrifuge. The machine is compound acting as the sepn. of the heavier soap stock is affected in the lower compartment and the lighter parts in the upper. The whole

operation of stopping, cleaning, and starting again can be done in 10 min. The yields obtained are from 1 to 8% better than by the gravity sepn. This method means not only a more rapid handling of oils, but permits of a compact installation. The oil can be run directly to the bleaching kettle. One machine will hold 450 lbs. of soap before it has to be cleaned and it can handle from 40 to 60,000 lbs. of oil per 24 hrs. Patent has been applied for on the process and the machine, a sketch of which is given.

E. SCHERUBEL

Manufacture of soaps from paraffin and similar hydrocarbons. WALTER SCHRAUTH AND PETER FREISENHAGEN. *Chem.-Ztg.* 45, 177-8(1921).—Soaps made from hydrocarbons were sold in central Europe during the war. In their manuf. autoclaves of 3000 kg. capacity equipped with agitators and able to withstand 20 atm. are used. A charge consists of 350 kg. beeswax, 300 kg. paraffin, 300 kg. ceresin, and 30 kg. NaOH in 100 l. of water. This is heated to 180° and at a pressure of 10 atm. The process is complete in 8 hrs., when the charge is withdrawn, mixed with water and coloring matter and perfume added. During the autoclave sapon. O is consumed; by keeping a pressure of several atm. of air in the autoclaves very satisfactory results were obtained. The finished product lathers freely and contains only 15 to 25% of unsaponified material, which emulsifies readily. The fatty acids sepd. by H_2SO_4 had a sapon. no. of 170 to 190. Twitchell reagent and "Kontakt" can be substituted as emulsifiers in the process and montan wax can be used in the place of beeswax and vaseline in place of paraffin.

E. SCHERUBEL

Washing compounds and washing tests. E. KEIT. Mannheim-Rheinlan. *Deutsch Washerei Ztg.; Seifensieder Ztg.* 48, 41-2(1921).—K. briefly mentions his method of making washing tests by using 1000 to 2000 napkins, towels and bed-sheets from large hotels—discarding abnormally soiled pieces and keeping the compn. of washing-liquor temp., time and preparatory treatment of wash uniform. Soaps of high rosin content produce a yellow tint in time, while washing compds. contg. trichloroethylene yield good results at first but develop a distinctly gray tint on the goods after they have passed 5 or 6 times through the laundry.

P. ESCHER

The refractometer in the factory laboratory (LÖWEN) 1. Catalysis in industrial chemistry (RIDGAL) 13. Manufacture of textile soaps and oil preparations for special work (GAUMNITZ) 25. Studies in emulsions. II. Reversal of phases by electrolytes and the effects of free fatty acids and alkalies on emulsion equilibrium (BHATNAGAR) 2.

Oil from copra. C. O. PHILLIPS. U. S. 1,369,265, Feb. 22. The extn. of oil from copra is improved by intimately mixing with the copra a small amt. of a dil. alk. substance, e. g., $NaHCO_3$ soln., preliminary to heating and pressing.

Iodine compounds of fatty acids. T. TAKAGI. Japan 36,162, April 12, 1920. From 15 to 20 parts of I are dissolved in 75 parts of fatty oil (cod-liver oil, olive oil, peanut oil, etc.) by heating at 50° with agitation. This is then heated for 1 hr. or more at 150° with 25 parts of cineole in a closed vessel. After cooling, it is mixed with 100 parts of 5% KI soln., shaken and set aside at 0°. The wax is sepd. and washed with H_2O . The product is not viscous. It is suitable for a food, having no taste of I.

Catalysts for hydrogenating. C. ELLIS. U. S. 1,369,013, Feb. 22. A catalytic material is produced by the reduction of an oil-sol. metal compd. of a weak org. acid, e. g., Ni oleate. The oil-sol. material may be dissolved in oleic acid or other unsatd. oily substances and the mixt. passed through a tube of considerable length lined with catalytic metal. A current of water gas or other reducing gas is passed in the opposite direction so that the entering oil meets water gas poor in H and the partially converted oil meets gas rich in H. The oil-sol. compd. of the catalytic metal is first reduced to

metal in the form of an oil-colloid and then serves as a catalyst for the hydrogenation of the oily material. It is stated that other catalysts may be similarly employed, e. g., Cu, Fe, Pd, Pt, Co, Cr, Mn, Ti, Mo or V.

Catalyzer for hydrogenation. S. UENO. Japan 36,170, April 15, 1920. The catalyzer is prepd. by heating C, obtained by dry distn. of the cellulose of fruits of the coconut palm or other substances, in a H_2 current. It is then made into a powder.

Regeneration of waste nickel catalyzer. K. OMURA and SUZUKI CO. Japan 36,200, April 15, 1920. Waste Ni catalyzer used for hardening oil is washed with C_6H_6 , aq. NaOH or Na_2CO_3 , the small quantity of oil remaining on the surface of the catalyzer, is washed with H_2O , dried and reduced by heating in a current of H. A more efficient catalyzer is produced than that newly prepd., the remaining oil promoting the action.

Soap for fats and grease. J. YASUI. Japan 36,166, April 14, 1920. 500 g. fatty oil are saponified with 30% NaOH and made into a homogeneous paste with 200 g. EtOH, which is heated with 700 g. naphtha under a reflux and cooled.

28—SUGAR, STARCH AND GUMS

F. W. ZERBAN

Hawaiian Sugar Planter's Association. Report on manufacturing machinery for 1920. *Louisiana Planter* 66, 138-40(1921).—This report deals with (1) the handling of crushed cane in its course through the mills, (2) the screening of juices, (3) clarification, and (4) machinery dealing with by-products. C. H. CHRISTMAN

Cane sugar in Mexico. F. D. CANFIELD AND A. G. RIOS. *Louisiana Planter* 66, 11-15(1921).—The possibilities of Mexico as a producer of cane sugar are large. Internal strife and lack of capital have prevented its development. Yields of 40 tons of cane per acre are the average. Details of the factory processes are given.

C. H. CHRISTMAN

Advances in beet-sugar manufacture during 1920. EDMUND O. VON LIPPMANN. *Chem.-Ztg.* 45, 181-2(1921).

E. J. C.

The cossette leaching apparatus "Rapid." K. V. ZIALECKI. *Listy Cukrovar.* 38, 268-71(1920); *Z. Zuckerind. Cechoslov. Rep.* 44, 315-8(1920).—Z. does not consider the apparatus an improvement over the diffusion system. Results obtained were inferior from both the chemical and the mechanical standpoints.

JOHN M. KENO

Chlorine balance during sugar manufacture, and the chlorine content of the beet. EMILE SAILLARD. *Compt. rend.* 172, 283-4(1921).—Continuing his researches on the different constituents of the beet (cf. C. A. 12, 1933; 14, 1764) S. made volumetric Cl detns. on factory products and on the different parts of the beet. The figures vary somewhat from yr. to yr. The beet contains an av. of 0.016% Cl, beet molasses 0.3%. 80% of the Cl in the beet passes into the molasses, 19% into the exhausted chips, and 1% is undetd. loss. In samples of beets containing 17% sugar the Cl was found to be distributed as follows: Leaf blades 1% Cl on total solids, leaf stalks, including the mid rib, 1.8%, necks 0.34%, beet itself 0.08%. Fodder beets gave similar results.

F. W. ZERBAN

Some analytical data on the sugar beets cultivated in Roumania. G. I. BABORANU. *Bull. soc. chim. România* 1, 84-6(1919).—In the old Roumanian territory, the sugar beet is cultivated on a reduced scale for the necessities of three sugar factories. A table is given with comparative analytical data for different sugar beets cultivated in the country.

M. WEINBERG

Points on Steffen-house practice. WALLACE MONTGOMERY. *Sugar* 23, 125-6(1921); cf. C. A. 15, 186.—The quantities of material in process at various stages in a Steffens house are indicated. Calcs. are shown.

C. H. CHRISTMAN

The Martel filter and its operation in Louisiana. ANON. *Louisiana Planter* 65, 395(1920).—A special filter press is described. Its use in connection with Filter-Cel gives clarification of cane juice which compares favorably with the older lime-sulfur process.

C. H. CHRISTMAN

One of the methods of producing white granulated sugar in Louisiana. ANON. *Louisiana Planter* 65, 396-7(1920).—A brief description of the procedure used is given. Special attention is directed to a set of continuous settling tanks. A diagram of this feature is shown.

C. H. CHRISTMAN

Design of sugar centrifugal baskets. BRUNO C. LECHLER. *Sugar* 23, 11-3(1921); cf. C. A. 14, 473.—The factors which cause loss of energy in the operation of sugar centrifugals are enumerated. B. then proposes a general rule for the application of power to centrifugals in batteries and singly. Direct drives are recommended as being most efficient. The suggestion is offered that the continuous centrifugal will eliminate present losses.

C. H. CHRISTMAN

An arrangement for the production of artificial frothing for the purpose of obtaining better circulation of liquors in evaporators. ASKAN MÜLLER. *Z. Zuckerind. u. echoslov. Rep.* 44, 231-5(1920).—The circulation is aided by the production of steam bubbles which carry the juice upward. Disks covering the heating tubes retard the escape of the smaller bubbles into the vapor space, resulting in a very rapid internal circulation of the juice.

JOHN M. KRNO

Working up sirups into after-products. KAREL URBAN. *Listy Cukrovar.* 38, 197-206(1920); *Z. Zuckerind. Cechoslov. Rep.* 44, 207-12, 215-20(1920).—An extensive review of Claassen's work on the production of after-products from centrifugal sirups is given. During the 1920 campaign U. noticed that the sirups desugarized at a much slower rate than in previous years. With sirups from partly frozen beets, incrustation of the evaporator tubes by the decompn. products present caused a great deal of trouble during boiling. The best finishing temp. for the crystallizer work is 45°. The av. decrease in the purity of the sirup was 4%, for 10 hrs. 0.4%. In a normal year this decrease would be 5-8%, for 10 hrs. 0.5-0.6%. For control work during the boiling in vacuum the refractometer was found exceedingly useful. A specially constructed Zeiss instrument was used for this purpose to avoid difficulties due to foaming. The speed of crystn. also was controlled by this instrument. Other useful control tests are described and discussed.

JOHN M. KRNO

Vegetable decolorizing carbons. A. B. BRADLEY. *Intern. Sugar J.* 23, 25-32 (1921); cf. C. A. 14, 652.—B. has detd. the decolorizing effect of ten different carbons on a 50% soln. of a Jamaican raw sugar, the speed of filtration obtained, also the size of grain and the apparent sp. vol. of some of them. For 5 of the carbons the decolorizing power and speed of filtration upon repeated use, without revivification, were also observed. For comparison similar tests were made with 2 other raw sugars. The results are summarized as follows: The greatest decolorizing effect is produced by carbons giving the quickest rate of filtration. The activity of a vegetable decolorizing carbon is not dependent on the % of C present. The carbons containing the largest % of the finest grain gave most trouble during filtration, and the lowest decolorizing results. The more porous the carbon, the greater is its decolorizing effect and rate of filtration. The sp. vol. is not entirely dependent upon the compn. of the sample as regards size of grain. Equal vols. of different samples of decolorizing C of the same grain size do not give similar decolorizing effects, the efficiency being influenced by the porosity of the sample. Decolorizing carbons, if used for treating successive batches of sugar sirup, without revivification, seem to choke up, first according to the amt. of dust they contain, and finally according to the % of large grain. Samples containing the max. quantity of medium grain (84-106 mesh) hold up best. Carbons containing high % of finest grain

give better results with high grade sugars than larger-sized carbons. On raw sugars inclined to be gummy, better results are obtained with carbons of uniform medium grain. Large-grained carbons give good results only when used in large quantities.

F. W. ZERRAN

Analysis of the damaged granulated sugar brought from Iaffa (Palestine). G. I. BABOIANU. *Bull. soc. chim. România* 1, 86-7(1919).—This sugar having been transported on the sea in unfavorable conditions has absorbed moisture and been partly inverted. A table is given with comparative analytical data for this sugar. It contains 3-4% moisture, 2.15-2.94% reducing sugars, 0.12-1.52% organic impurities. Polarization: 91.90-93.74. It has been reworked and recrystallized, the commercial yield ranging between 85.04 and 89%.

M. WEINBERG

Chemical control results obtained in a Queensland mill. J. F. FOSTER. *Intern. Sugar J.* 23, 52(1921).—Annual report of the Mulgrave Central Mill Co. for 1919. An extn. of 93.43% was obtained, with 33.37% maceration. The mixed juice had a purity of 85.59. The sucrose losses were 6.57% in bagasse, 0.53% in press cake, 9.49% in molasses, and 4.61% undetd.

F. W. ZERRAN

An inherent error in certain modifications of the Clerget method of double polarization. C. A. BROWNE. *Louisiana Planter* 66, 109(1921).—B. criticizes the assumption that const. salt concn. in sugar solns. gives const. physical chemical effects with varying amts. of sucrose. The use of invertase is recommended as introducing the least source of error.

C. H. CHRISTMAN

The application of the Clerget method to dilute sucrose solutions. R. F. JACKSON AND C. L. GILLIS. *Louisiana Planter* 66, 141-2(1921).—Reply to Browne (preceding abstract). J. and G. claim that the effect of salt in the same concns. is of the same order on both sucrose and invert sugar. Their measure of sucrose is given as the algebraic difference between the direct and invert polarizations. Using pure sucrose solns. of known strength, their analyses agree within 0.01%.

C. H. CHRISTMAN

A few observations upon the Clerget modification of neutral polarization. C. A. BROWNE. *Louisiana Planter* 66, 171-2(1921).—Reply to Jackson and Gillis (preceding abstract). Browne criticizes the method of J. and G. because it does not apply without error to the analysis of complex mixtures. Certain inaccuracies in the tables and formulas proposed by J. and G. are discussed.

C. H. CHRISTMAN

The analysis of sugar mixtures containing two monosaccharides. C. A. BROWNE. *Intern. Sugar J.* 23, 35-8(1921).—The reducing ratios of two monosaccharides (cf. *J. Am. Chem. Soc.* 28, 439(1906)) detd. by one and the same method are practically const. for amts. between 50 and 250 mg. of sugar. Even for different methods, like those of Allihn and of Kjeldahl, they differ very little. With smaller amts. of sugar than 50 mg. the ratio becomes lower; the ratios between monosaccharides and reducing disaccharides are not very const. The reducing ratios, calcd. by Van der Haar (book) for Schoorl's method (*C. A.* 14, 2561), by avg. only the ratios for 2 extreme quantities, are too high. In reality they closely approach the ratios found for Allihn's and Kjeldahl's methods. Schoorl's method of detg. reducing sugars has the disadvantage of being adapted only for up to 90 mg. of sugar; for this reason Allihn's method is preferable.

F. W. ZERRAN

Determination of lime salts in juices by means of a standard soap solution. WALLACE MONTGOMERY. *Intern. Sugar J.* 23, 39-42(1921).—4.357 g. pure crystd. $\text{BaCl}_2 \cdot 2\text{H}_2\text{O}$ are dissolved in water to 1000 cc.; 25 g. Castile soap shavings are dissolved in 60% alc., and made up with water to 1000 cc. The soap soln. is standardized by placing 10 cc. of the BaCl_2 soln. in a 4-oz. oil sample bottle, dilg. to 50 cc. with water, and running in the soap soln. until a foam 1 in. high will remain for 5 min. 10 cc. of the soap soln. are to correspond to 10 cc. of the BaCl_2 soln., which in turn are equivalent to 0.01

g. CaO. Since it takes 0.5 cc. of soap soln. to produce the foam on 50 cc. of water, the soap soln. must actually be made of such strength that 10.5 cc. of it will react with 10 cc. of BaCl₂ soln. The same correction of 0.5 cc. must be applied to results of detns. For Ca detns. in sugar-house products any free acid must first be neutralized exactly with NH₄OH. 20 cc. of thin juices, and 10 cc. of sirups and molasses are used for analysis, and in each case dild. to 50 cc. Two tables are given, showing g. of CaO per 100 total solids, corresponding to the cc. of soap soln. used.

F. W. ZERBAN

Burning bagasse for fuel. F. I. SCARD. *Sugar* 23, 37-8(1921).—S. outlines the data required to det. the efficient working of boilers when bagasse is used as fuel. He computes the B. t. u. content of bagasse from the formula

$$\frac{(F \times 8556 + S \times 7119) - W \times 1100}{100}$$

where *F* is % fiber, *S* is % sucrose and *W* the % water. 65% of the heat value of bagasse should be utilized in efficient boiler practice. The data furnished by flue gas analysis should be utilized in obtaining efficient results.

C. H. CHRISTMAN

Compressed yeast as a sugar by-product. HENRY ARNSTEIN. *Sugar* 23, 72-3 (1921).—A. proposes the use of molasses in place of the more expensive malted grain in the production of yeast. The yield of 4½ lbs. compressed yeast and 64 proof gallons of alcohol from each gallon of molasses is given.

C. H. CHRISTMAN

Tucuman Agricultural Experiment Station's Annual Report for 1919. *Louisiana Planter* 65, 412-3(1920).—This is a condensed statement of the work done at the Tucuman Station.

C. H. CHRISTMAN

A study of the losses caused by delay in harvesting burnt cane. J. A. VERRITT *et al.* *Louisiana Planter* 66, 43-4(1921).—On selected plots cane was burned; some was cut at once and some left uncut until required for milling. After 15 days the cane left standing had lost 29.18% in wt. and 48.80% of its sugar content and the cut cane had lost 20.99% wt. and 51.66% sugar. Little difference is found between burnt cane cut at once or later.

C. H. CHRISTMAN

The treatment of cane damaged by frost. WM. E. CROSS. *Louisiana Planter* 65, 363-6(1920).—Damage to cane by frost depends upon the duration and intensity of the frost and subsequent weather conditions. Decomn. follows from enzymes present in the plant and bacteria from outside sources. Topping and windrowing are recommended for most canes, but certain varieties show less decomn. when left standing until ready for the mill. Care must be utilized to prevent fermentation of the juice before clarification. The use of soda ash to neutralize acidity due to fermentation is said to permit greater ease in handling the soured juice. High sulfitation gives better clarification and the use of kieselguhr is advised. Badly damaged cane can be utilized for the production of alcohol or cattle feed. Great care must be exercised in chemical control in order to direct efficient plant operation.

C. H. CHRISTMAN

Statistics of the distribution and yield of cane varieties in the season of 1919. PR. VAN HAREVELD. *Arch. Suikerind.* 28, 2095-176(1920); cf. *C. A.* 14, 653, 2870.—Complete data are given for 173 out of 179 factories. In point of acreage planted 247B is still first (28.5%), but EK 28 has moved from third to second place (22.5%), and 100 POJ from second to third (16.75%). The old standard variety Black Cheribon has become unimportant. In the order of sugar produced per acre by the 3 principal varieties EK 28 is still first, followed by 100 POJ and 247 B.

F. W. ZERBAN

Fungi and cane germination. C. W. EDGERTON AND C. C. MORELAND. *Sugar* 23, 16-7(1921).—These authors enumerate the various fungi found on sugar cane. The relation of these fungi to various diseases of cane is pointed out. A fall of 50% in the germination of seed cane follows infestation by fungi. Expts. in disinfecting with formaldehyde and corrosive sublimate have given encouraging results.

C. H. C.

The mosaic or mottling disease of the sugar cane. C. A. B. *Intern. Sugar J.* 23, 12-9(1921).—A digest of recent literature on the subject, with bibliography.

F. W. ZERBAN

Industrial and agricultural chemistry in the British West Indies (BROWNE) 13. The hyposulfites (DUBOSC) 6. The refractometer in the factory laboratory (LÖWEN) 1. Action of light on the sugar content of the beet (COLIN) 11D. Influence of clear weather on beets (ZAMARON) 11D. Explosion from sugar dust (ANON.) 24.

LANGEN, FELIX: Die Arbeitsweise der Zuckerraffinerien. Magdeburg: Schalehn & Wollbrück, 1919. M. 60.

Crystalline sugar from honey. M. YUWATA. *Japan* 36,201, April 15, 1920. A dil. soln. of honey is mixed with animal charcoal, filtered, and concd. above its solidifying point by evap. *in vacuo* at a low temp. The sirup is vigorously agitated while hot, satd. with air, mixed with 3-6% cold H₂O and set aside at below 10°. Cryst. sugar is produced.

29—LEATHER AND GLUE

ALLEN ROGERS

Chrome leather analysis. II. R. F. INNES. *J. Soc. Leather Trades' Chem.* 4, 294-300(1920); cf. C. A. 14, 1059.—The committee calls attention to remarkably concordant results obtained by its previously reported method for the detn. of Cr, and suggests the adoption of this as the official method of the British section. Brief reports are made on methods for other detns. A discussion of the effect of soap in fat-liquoring is appended. In soap fat-liquoring chromed goat skins an acid chrome soap is formed which is not wholly extd. by petroleum ether. In analyzing fat-liquored skin one cannot estimate the soap by extg. with H₂O as a H₂O-sol. soap is no longer present. Na and K soaps with the same proportion of fatty acids give the same kind of leather, the alkali being largely a carrier of the fatty acids. C. F. JAMESON

Recent research in leather manufacture. H. R. PROCTER. *J. Soc. Leather Trades' Chem.* 4, 282-90(1920).—P. fears that much important research in leather manufacture is little understood by those whom it is designed to benefit, and in this paper he attempts to remedy this to a slight extent. He reviews recent important advances such as: Stiasny's discovery of the syntans, his own discovery that chrome tannage may be stripped in the cold by solns. of salts of dibasic acids, Nance's vacuum tanning process, the method of preparing "chrome extract" by direct reduction of Na₂Cr₂O₇ with H₂SO₄, the use of viscous colloids as vehicles for the tanning extract, etc. Particular attention is called to Meunier's investigations on tannage with chem. substances, especially quinone. Referring to further work of M. with phenol derivs. such as pyrogallol and gallic acid, P. discusses the oxidizing effects of the air on tannages of this sort. He mentions Wilson's new method for the detn. of tannin, and states that although the official method may be imperfect, no changes can be lightly undertaken. In the vegetable tanning process some of tannins are in mol. soln. but most of them are colloidal with but little power of chem. combination. The colloidal particles of tannins have negative charges. Hide in acid soln. is positively charged. When the two meet they combine. In alk. soln. the hide is negatively charged, this cannot take place, and tanning does not occur. This is the condition in the early stages of the tanning process, but later when the electric charge of the hide is nearly saturated, fixation still takes place, adding wt. and solidity to the leather. Fixation also takes place on

drying and on aging, by reason of the oxidation of tannins and non-tannins in the hide.

C. F. JAMERSON

Extraction of grease from leather. ANON. *J. Soc. Leather Trades' Chem.* 4, 300-3(1920).—The committee has investigated the behavior of different solvents of grease on leather fat-liquored in different ways, and proposes that either CHCl_3 or C_6H_6 be officially recognized as the solvent in all defns. of grease in leather. If color of the ext. is considered important the use of C_6H_6 is recommended.

C. F. J.

Examination of Roman leather. J. ATKIN AND R. H. MARRIOTT. *J. Soc. Leather Trades' Chem.* 5, 10-4(1921).—Roman leather excavated on the site of an old fort, 7½ feet below the present ground level, examined under the microscope is shown to retain its characteristic structure. The degree of tannage is 45, which compares very favorably with modern vegetable-tanned upper leather. Investigation shows that the untreated leather has practically no fertilizer value.

C. F. JAMERSON

Acid unhairing. R. H. MARRIOTT. *J. Soc. Leather Trades' Chem.* 5, 2-9(1921).—Pieces of hide were unhaired by the aid of dil. acids with or without the addition of neutral salts. Observations were as follows: (1) The depilatory action is not bacterial; (2) this method of unhairing is not as effective as liming; (3) there is an action similar to that of bating; (4) the acid liquor appeared to contain unhydrolyzed gelatin; (5) a ferment which produces alc. developed in the liquor; (6) unbaiting is probably due to the hydrolytic action of the acid on some prosthetic protein similar to mucin, its carbohydrate group being attacked by the ferment.

C. F. JAMERSON

Investigation of the causes of "run" pelts in the sweating process. P. HAMPSHIRE. *J. Soc. Leather Trades' Chem.* 5, 20-6(1921).—The examn. of "run" pelts damaged in the sweating process shows injury to be due to nematodes. They are not present in the skins on arrival at the tannery, but are found in the sweating chamber itself.

C. F. JAMERSON

Skin structure and bating. A. SEYMOUR-JONES. *J. Soc. Leather Trades' Chem.* 4, 291-3(1920).—All flayed skins consist essentially of two distinct parts, the epidermis and the dermis. After unhairing the dermis is left. After fleshing, the pelt is made up of four distinct layers, the grain membrane, the grain, the fatty layer, and the corium. By applying trypsin in the form of a paste to the grain of a skin, previously delimed with CH_3COOH , the mass of elastic fibers is digested. The grain later becomes flaccid and the main effect of bating is accomplished. Bating should be performed in three operations in practice, (a) deliming by means of acid; (b) reduction of the grain and grain membrane by the use of trypsin; (c) removal of fat from the fatty layer (a satisfactory method is yet to be evolved; the use of lipase may offer a solution).

C. F. JAMERSON

Tannin content of the fruit of the guayacan of the Argentine Republic (*Caesalpinia melanocarpa* Gris.). FIDEL ZELADA. *Informes depl. investigaciones ind. Univ. Tucuman* No. 12, 3-11(1920).—Fruits with a moisture content of 25% yielded 29.7% of tannin. By a number of tests it was shown that the tannin obtained is probably identical with that from nutgalls.

L. E. GILSON

Gonakie from Senegal. F. HEIM, et al. *Industries du cuir* 1920, 306; *J. Soc. Leather Trades' Chem.* 5, 36(1921).—This is the local name for *Acacia arabica* Willd. The pods contain when dug 40-45% of hard dark brown seeds, and 55-60% of husk, very rich in tannin. Analysis of the whole seeds gave 26.53% tannin, 12.45% non-tannins, 51.02% insolubles and 10% moisture. The ash content is 4.52% consisting of silica, traces of Mn, Fe and Mg with a large proportion of Al. Other analyses show from 18.02 to 31.70% tannin. Iron alum gave a blue-black color.

C. F. JAMERSON

Guides to analysis. IV. Interpretation of glue analysis. CHAS. R. MCKEE. *Chem. Bull.* (Chicago) 8, 66-7(1921).—"A routine series of tests and analyses of glue

will not fully det. its value for all purposes, as it is equally important that the purpose and conditions of use be studied." Thus a certain factory although unable to make satisfactory airplane propellers with officially certified glue, made with another grade propellers answering all other requirements. It would be absurd to apply woodworking specifications as a general standard, for example, to that used for rubber, wallpaper, and abrasives. Various tests are commented on as follows: *Viscosity and jelly strength*. Used as a main guide in detg. quality. *Foam test*. Has relation to behavior in spreading machines. *Grease*. May or not be objectionable. Det. by careful hydrolysis with acid, mixing residue with sand and extg. *Nitrogen*. Not a guide to grade. *Ash*. Shows defective manuf. or in rare cases, adulteration. *Sand sulfides*. Must be avoided where glue is used for silverware wrappings. *Joint test*. All good glues properly used give a joint stronger than wood itself; this test, therefore, reflects condition of the wood, contact of surfaces and manipulation. *Appearance, fracture and glass chipping*. All without value. *Film test*. Difficult to control.

JEROME ALEXANDER

Pelt and fur dyeing (FUCHS) 25.

Uniting rubber with leather. S. O. HAHN. U. S. 1,369,240, Feb. 22. Ordinary com. rubber cement, after having been deprived of a portion of its S content, is forced into leather so as to impregnate it beneath the surface and rubber is subsequently vulcanized to the leather to provide a firm union between the materials.

30—RUBBER AND ALLIED SUBSTANCES

JOHN B. TUTTLE

Tentative specifications for insulated wire and cable: 30 per cent. Hevea rubber. ANON. *Proc. Am. Soc. Testing Materials* 20, 1, 736-47(1920).—Specifications cover (a) conductor, (b) insulation, (c) inspection of insulated wire, of the 30% *Hevea* type. Chem. analysis is to be made according to the Joint Rubber Insulation Committee procedure (cf. C. A. 11, 899), but the formula for calcg. the rubber hydrocarbons has been changed, and the method for total S given in the preliminary report of the committee (cf. C. A. 8, 1214), is used in place of the one recommended by the committee in its final report.

J. B. T.

The determination of factis in rubber. P. DEKKER. *Gummi Ztg.* 35, 212(1920).—The editors of *Gummi Ztg.* (35, 52(1920)) have criticized the paper of Dekker (cf. C. A. 14, 2872). They claim that the indirect method for the detn. of factis, based upon wt. decrease upon extn. with alcoholic liquor, is more advantageous than the direct; and that a more reliable detn. can be made when the rubber is not subjected to a preliminary swelling in C_6H_6 . The reasons assigned for the belief that the Dekker method is faulty, are: The material is washed with alc. and hot water; the saponif. liquor will not penetrate rubber swollen with C_6H_6 ; and this liquor, which would dissolve a portion of the rubber, is decanted off. D. holds that the indirect method must be in error since oxidation of the extd. rubber takes place; and further takes issues with the editors on all of the other points. D. states that all methods are unreliable in the presence of asphalt, whereas *Gummi Ztg.* states that with suitable methods, the detn. of factis in the presence of asphalt can be accomplished.

ALAN LEIGHTON

Recent progress of the rubber industry. KAICHI KAWAKAMI. *J. Chem. Ind. (Japan)* 23, 644-59(1920).—This is a review of important progress of the world's rubber industry during the last 10 years. In Japan there was used per capita during 1917 only 0.12 lb. as against 4.1 lb. in the U. S. 8.7% of the raw materials is now supplied by cultivated plants. Geographical distribution and the amt. of the production of these materials; processes for detersination, coagulation and maturation, are considered.

The theory of tackiness of crude rubber, thermal study of the rubber, chemistry of vulcanization, and various processes of artificial rubber industry are discussed in detail.

S. T.

The oxidation of rubber. F. KIRCHHOFF. *Gummi Ztg.* 35, 191(1920).—Dekker (cf. *C. A.* 14, 2872) has called attention to the fact that extd. rubber is easily oxidized and that this causes an error when the fact is detn. is made indirectly. K. points out that he called attention to this several years ago (*C. A.* 7, 4083). ALAN LEIGHTON

The relative activity of various allotropic forms of sulfur towards caoutchouc. D. F. TWISS AND F. THOMAS. *J. Soc. Chem. Ind.* 40, 48-50T(1921).—A study of the reactions between caoutchouc and 3 forms of S, (a) S_A, (b) S_M, (c) S_R. S_A and S_M under ordinary conditions behave alike, owing probably to the rapid change of S_M at the temp. of vulcanization into an equil. mixt. consisting of S_R and S_A. (Cf. *C. A.* 13, 2787.) By vulcanizing at lower temps. using aldehyde-ammonia the rate at which equil. is reached is reduced so as to enable a study to be made of the different vulcanizing capacities of the various forms of S. The expts. were (a) with finely powdered S sol. in CS₂ and consisting entirely of S_A; (b) extd. sublimed S, insol. in CS₂, consisting mainly of S_M. Vulcanization was effected at 98, 108 and 118°. S_M is inferior to S_A, the ratio being 1 to 1.4 at 98°, 1.3 at 108 and 118°. The temp. coeff. is fairly const. over the range 138-168°, through which range S_A gives a greater percentage of S_R, showing that S_A and S_M are of almost equal activity. A study of the relative activity of S_A and S_R was made at higher temps. by using synthetic rubber (from dimethylbutadiene). The course of the reaction was followed by the vulcanization coeff. The S enters into the reaction in approx. a rectilinear course. If this is caused by autocatalysis (cf. *C. A.* 13, 386), it is not caused in this case by the non-rubber constituents of natural rubber. The temp. coeff. is lower between 178 and 188 than between 168 and 178°, suggesting that the Sequil. at the higher temps. is less active than at the lower. Since the equil. at the higher temps. contains a higher proportion of S_M and S_R, and since S_R is found to be approx. equal to S_A, these results confirm those obtained at lower temps. that S_M is less active than S_A. [These results are diametrically opposed to those of G. van Iterson, who explained the increase in the rate of vulcanization by the formation of S_M from S_A. (Cf. *C. A.* 13, 386.)] [ABSTR.] J. B. T.

Note on the cold vulcanization process of Peachey. ANNE DUBOSC. *Rev. prod. chim.* 24, 48(1921).—D. claims priority over Peachey for the discovery of the vulcanizing effects of SO₂ and H₂S in the cold. A. P.-C.

Cold vulcanization of rubber by gases. S. J. PEACHEY. *Rubber Age* 8, 482(1921).—Reply to Dubosc (cf. preceding abstr.); cf. also *C. A.* 14, 2873; 15, 1089. J. B. T.

A new method for vulcanizing rubber. WILHELM. *Kunststoffe* 11, 17-8(1921).—A discussion of the patent of Peachey (*C. A.* 13, 3040). C. J. WEST

The regeneration of rubber in its technical and economic aspects. PAUL ALEXANDER. *Chem. Ind.* 43, 531(1920).—The paper is outlined as follows: (1) *The method of rubber regeneration*: There is no "best" method. The value of any method depends on the source of the material and the purpose for which the product is intended. (1) Sources of material for the technical recovery of regenerated rubber: (a) first rubber shoes, and later tires; (2) Problems of regeneration: (a) to restore the rubber to a plastic condition; (b) to sep. it from the fabric; (c) to sep. it from the mineral fillers. (3) Summary of regeneration method: (a) methods solely for restoring plasticity; (b) methods for sepn. of the rubber: (1) acid method, (2) alkali method; (3) soln. method; (4) mechanical method; (4) methods for removal of fabric: (a) decompn. of the fabric; (b) dissolving of the rubber; (c) a new mechanical sepn. method; (5) removal of mineral fillers: (a) not always necessary; (b) completely accomplished only by the soln. method; (6) classification of regenerated rubber; (7) estn. of the regenerated prod-

uct: (a) detn. of (1) content in mineral fillers, (2) content in acetone-sol. materials, (3) saponifiable portion, (4) content in bituminous material, (5) S used in vulcanization, (6) the content in rubber (by taking the difference); (b) importance of phys. tests; (c) sp. gr. of little value here; (d) danger of inaccurately designating the acetone-sol. material as "resin;" (8) methods of regeneration in the patent literature. (II). The economic significance of the reclamation of rubber. Germany seems to be abandoning the reclamation of rubber and the production of synthetic rubber. The decline of these industries is due to present conditions of the world rubber market, which make for such a plentiful and cheap supply of the raw material that the reclaimed and the synthetic products cannot compete. These conditions will not continue, however, and the certainty that the supply of raw rubber will in the future be unequal to the demand justifies the encouragement of rubber reclamation. Figures are given to show comparative prices of raw and reclaimed rubber.

ALAN LEIGHTON

Solvents and thinners used in the rubber industry. FREDERIC DANNERTH. *India Rubber World* 64, 487-9(1921).—A review of the specifications, properties and methods of testing some org. solvents. Cf. C. A. 14, 3338. J. B. T.

Proposed tentative specifications for rubber gloves for electrical workers. ANON. *Rubber Age* 8, 479-80(1921). J. B. T.

The manufacture of rubberized and rubber coated fabrics. FREDERIC DANNERTH. *Rubber Age* 8, 317-20, 364, 369(1921); *Color Trade J.* 8, 23-7, 102-5(1921).—A review of some technical processes. J. B. T.

Benzene poisoning in rubber manufacturing. ROBERT S. QUINBY. *Rubber Age* 8, 451(1921).—A review of the bulletin of the Rubber Assoc. of America on the use of benzene. J. B. T.

Substitutes for rubber tires. JAHR, BERLIN-LICHTERFELDE. *India Rubber World* 63, 417(1921).—The following substitutes for rubber tires are discussed, with diagrams: Bristle, fiber, cord, felt, hair, paper and cardboard and asphalt tires. The paper is not well given to abstracting without reproducing the diagrams. ALAN LEIGHTON

Preparation of isoprene from light camphor oil (NISHIZAWA) 10. Dyeing and its connection with the rubber industry (THOMPSON) 25. Uniting rubber with leather (U. S. PAT. 1,369,240) 29.

Tire-filler. V. CURTITA. U. S. 1,369,626, Feb. 22. A mixt. permeated with air-filled pockets and adapted for filling tires to impart resilience to them is formed of crude rubber 45-70, a filler 10-45, S or other vulcanizing material 3-20, PbO 0.5-30, (NH₄)₂CO₃ or other "leavener" 0.5-4 and tar or oil 0.5-3 parts.

